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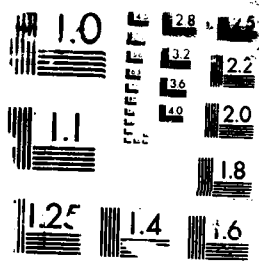
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METAL CONTACTS TO CADMIUM TELLURIDE (CdTe)

Final Technical Report

by

R H Williams and I M Dharmedasa

October 1987

United States Army

RESEARCH AND STANDARDIZATION GROUP (EUROPE)

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→ react with CdTe and with its native oxide, TeO_2 at room temperature. Ag shows an inert behaviour on TeO_2 . Although the reactions between noble metals are unexpected, a strong out-diffusion of Te is observed in these cases.

The macroscopic behaviour of the contacts was studied using conventional current-voltage and capacitance-voltage techniques. A large variation of Schottky barriers were observed for metals on CdTe and in particular two distinct values of barrier heights were observed for certain metal-CdTe systems. Ag, Sb and Au consistently produce two values of barrier heights with etched surfaces (0.72 and 0.93 eV) irrespective of their metal work functions. Ageing of the high barriers under normal atmospheric conditions reduce the rectification properties completely, due to increase in surface condition. This current contribution can be removed by isolating the diodes using chemical etching or any other means. Studies on thermal stability of metal-CdTe contacts show that they are unstable at temperatures above $\sim 250^\circ\text{C}$. Most stable and noise free contacts were obtained with Sb, and these diodes withstand annealing at $\sim 300^\circ\text{C}$.

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ABSTRACT

Metal-CdTe contacts, fabricated on three different CdTe surfaces were studied for a large number of metals. These surfaces were prepared by cleaving in ultra high vacuum, cleaving in air and etching in 1% bromine in methanol solution. The nature of these CdTe surfaces was investigated using ESCA, AES and SXPS techniques. The studies concentrated mainly on the more surface sensitive technique; SXPS, using synchrotron radiation of photon energy 100 eV. It has been found that the air-cleaved and chemically etched CdTe consists of TeO_2 on the surface. The most commonly used chemical etchant for CdTe, 1% bromine in methanol, preferentially removes Cd from the CdTe surface.

Microscopic interactions between evaporated metal and CdTe were monitored during the initial stages of interface formation using the SXPS technique. Au, Ag, Cr and Mn were selected for these studies; Au and Ag to represent the noble metals and Cr and Mn to represent more reactive metals. These studies reveal that almost all metals react with CdTe and with its native oxide, TeO_2 at room temperature. Ag shows an inert behaviour on TeO_2 . Although the reactions between noble metals are unexpected, a strong out-diffusion of Te is observed in these cases.

The macroscopic behaviour of the contacts was studied using conventional current-voltage and capacitance-voltage techniques. A large variation of Schottky barriers were observed for metals on CdTe and in particular two distinct values of barrier heights were observed for certain metal-CdTe systems. Ag, Sb and Au consistently produce two values of barrier heights with etched surfaces (0.72 and 0.93 eV) irrespective of their metal work functions. Ageing of the high barriers under normal atmospheric

conditions reduce the rectification properties completely, due to increase in surface conduction. This current contribution can be removed by isolating the diodes using chemical etching or any other means. Studies on thermal stability of metal-CdTe contacts show that they are unstable at temperatures above $\sim 250^{\circ}\text{C}$. Most stable and noise free contacts were obtained with Sb, and these diodes withstand annealing at $\sim 300^{\circ}\text{C}$.

1.0 INTRODUCTION

The n-type CdTe single crystals used in this work were of low resistivity (1 - 10 Ωcm) with carrier concentrations in the range 10^{16} - 10^{17} cm^{-3} . They were grown by either the fast vertical Bridgman method or the solvent evaporation technique. Some of the n-CdTe wafers used were obtained from Eagle-Pitcher Industries Inc, USA. Most of our work was on the two most reproducible types of CdTe surfaces, namely clean-cleaved and air-cleaved surfaces. However, the chemically etched CdTe surfaces are more technologically important in thin film and large area devices, and in many other practical applications. Therefore these surfaces are also investigated in detail. In this report the experimental results are given as a summary, and the relevant publications should be referred to for detailed descriptions. The publications resulting from this work are attached to this report and listed in the reference section.

2.0 EXPERIMENTAL

Atomically clean surfaces (110) were obtained by cleaving the crystals at a pressure of $\sim 10^{-10}$ Torr. Air-cleaved surfaces (110) were prepared by cleaving the crystals in air and exposing them to the laboratory air environment for at least 24 hours. The etching procedure consisted of immersing the sample for a few minutes in a 1% bromine in methanol solution followed by thorough rinsing in methanol. The nature of the CdTe(110) surfaces produced by the above methods was studied by the ESCA, AES and SXPS techniques. The stoichiometry of the surfaces was determined by comparing the relative heights of Cd and Te peaks. The presence of other

chemical species was also identified using the various spectral features and observed chemical shifts.

Microscopic interactions at metal-CdTe (110) interfaces were monitored as a function of metal film thickness by SXPS using the synchrotron radiation source at the Daresbury laboratory UK. Metal was evaporated from a metal loaded tungsten filament in ultra high vacuum and the thickness of the layer was measured using a quartz crystal film thickness monitor. A photon energy of 100 eV was chosen in order to achieve high surface sensitivity of photoemission ie. very short electron escape depths (typically 3 - 6 Å). Photoelectron energy distribution curves were recorded after each evaporation using a double-pass cylindrical mirror analyser with a resolution in the range (0.15 - 0.30) eV.

The AES spectra were also recorded in the same system, but at the beginning and at the end of the experiment only. AES were not taken during the SXPS experiment in order to minimise the possibility of intermixing at the interface due to the influence of the electron beam, since it is known that the CdTe surface is unstable under such conditions (Humphreys et al 1980, Sinclair et al 1981).

Finally the transport properties of the metal-CdTe junctions, made on all three surfaces, were investigated for a large number of metals. Metal-CdTe junctions were formed by evaporating thick layers of metal and studied by (I-V) and (C-V) techniques. The (I-V) characteristics were measured using a Keithley 230 programmable voltage source, a Keithley 617 multimeter and a micro computer. The (C-V) characteristics were measured at a frequency of 1 MHz, in the voltage range 0.5 to -4.0 V, using a Boonton 72B C-V meter and a microcomputer.

3.0 RESULTS.

3.1 SURFACE ANALYSIS BY ESCA, AES and SXPS

The chemical nature of the CdTe(110) surfaces produced by the three different methods was investigated using ESCA, AES and SXPS techniques. The results are shown in figures 1, 2, & 3 respectively. ESCA results for clean cleaved, air-cleaved and bromine methanol etched CdTe surfaces, using Al K α (1486 eV) radiation are shown in fig 1. These studies reveal (for details, ref 5) that the presence of C and O on air cleaved and chemically etched surfaces. Our recent studies confirm that most of the C seen on the surface is introduced during baking of the vacuum system, and not by the surface preparation method. The most common oxide present on these surfaces is TeO₂, as is shown clearly in the chemical shifts of Te 3d core level emission. Comparison of the Te 3d emission intensity (oxidized + unoxidized) with the Cd 3d emission intensity for oxidized and clean surfaces reveals that the air cleaved surfaces are stoichiometric in Cd and Te and the chemically etched surfaces are slightly enriched in tellurium(see table 1).

The typical AES spectra from clean cleaved, air-cleaved and 1% bromine methanol etched CdTe surfaces are shown in fig 2. Cl peaks at ~100 eV, seen for air-cleaved and chemically etched surfaces are due to contamination from the chamber during this experiment. Both air-cleaved and chemically etched surfaces are contaminated with carbon, and most of these are again introduced during baking of the vacuum system. The presence of oxygen on air-cleaved surfaces was clearly observed, but minimal oxygen was observed on

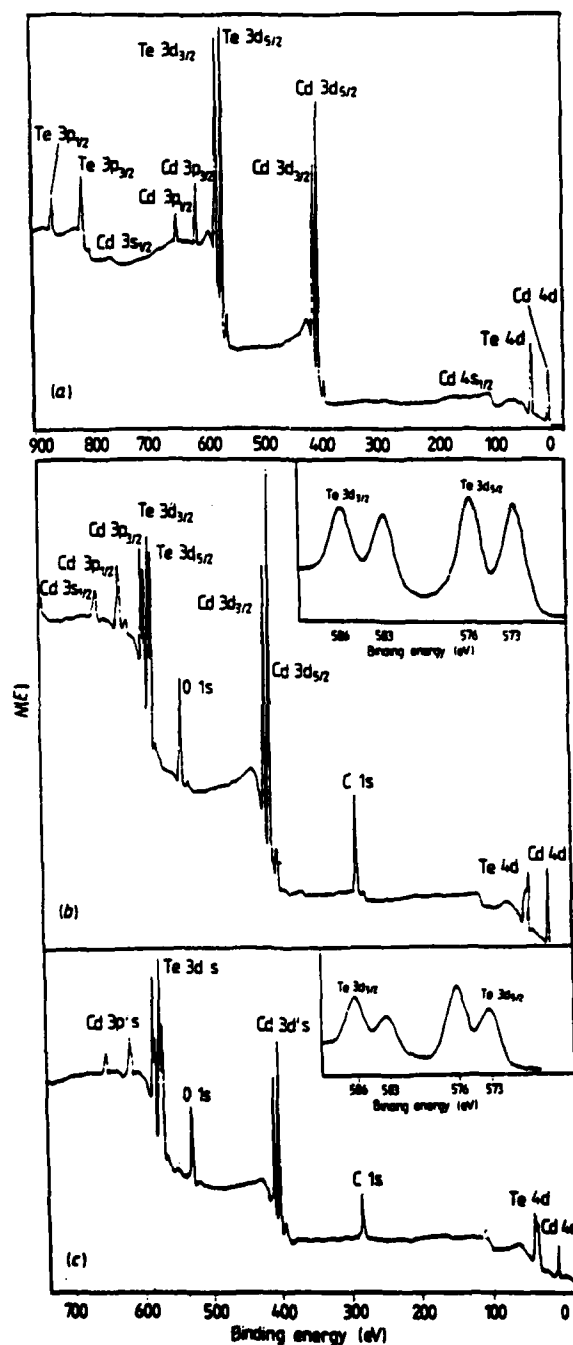


Figure 2. X-ray (Al K α , 1486 eV) induced photo-electron spectra of (110) surfaces of CdTe: (a), cleaved in an ultra-high vacuum of $\sim 10^{-10}$ Torr; (b), exposed to air for 48 h; and (c), etched in 50% bromine in methanol solution.

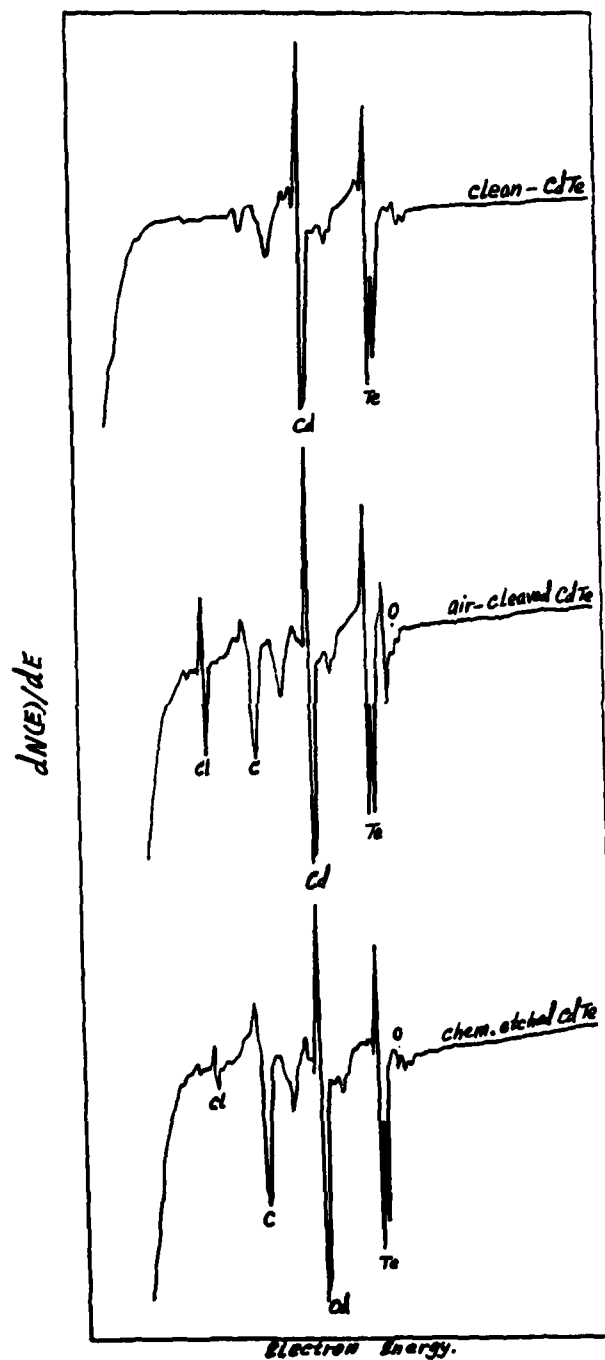


FIGURE 2. Auger spectra from (a) Clean - cleaved (b) air - cleaved (c) bromine methanol etched CdTe(110) surfaces.

chemically etched surfaces. The relative intensities of Te and Cd emissions (see table 1) show that the bromine methanol etched surfaces are rich in Te.

In fig 3 we show SXPS spectra ($h\nu = 100$ eV) corresponding to the Te 4d core level emission for four different CdTe surfaces. Figures 3(b), 3(c) and 3(d) represents the results obtained for lightly oxidized surface (cleaved and exposed to air for 1 hour), heavily oxidized surface (cleaved and heated in air) and a surface which has been freshly etched in 1% bromine in methanol respectively. All three surfaces contain TeO_2 (labeled on figures) with thickness depending on the preparation conditions. Relative amplitudes of the oxidized and the unoxidized Te components enable the thickness of the oxide to be estimated. In figures 3(c) and 3(d) these are equivalent to thicknesses of $\sim 3\text{\AA}$ and $\sim 1\text{\AA}$ respectively. Comparison of the Te 4d emission intensity (oxidized + unoxidized) with the Cd 4d emission for etched and clean surfaces enables the stoichiometry of the surface region to be estimated. These studies demonstrate that the chemically etched surfaces are close to stoichiometric in Cd and Te, but with a slight excess of Te (see table 1).

TABLE 1
Intensity ratios of Cd and Te for various CdTe surfaces as measured from different techniques.

surface treatment	ESCA Cd : Te	AES Cd : Te	SXPS Cd : Te
clean - cleaved	0.94 : 1.00	1.12 : 1.00	0.23 : 1.00
Air - cleaved	1.00 : 1.00	-----	0.22 : 1.00
Br_2 meth: etched	0.89 : 1.00	1.00 : 1.00	0.20 : 1.00

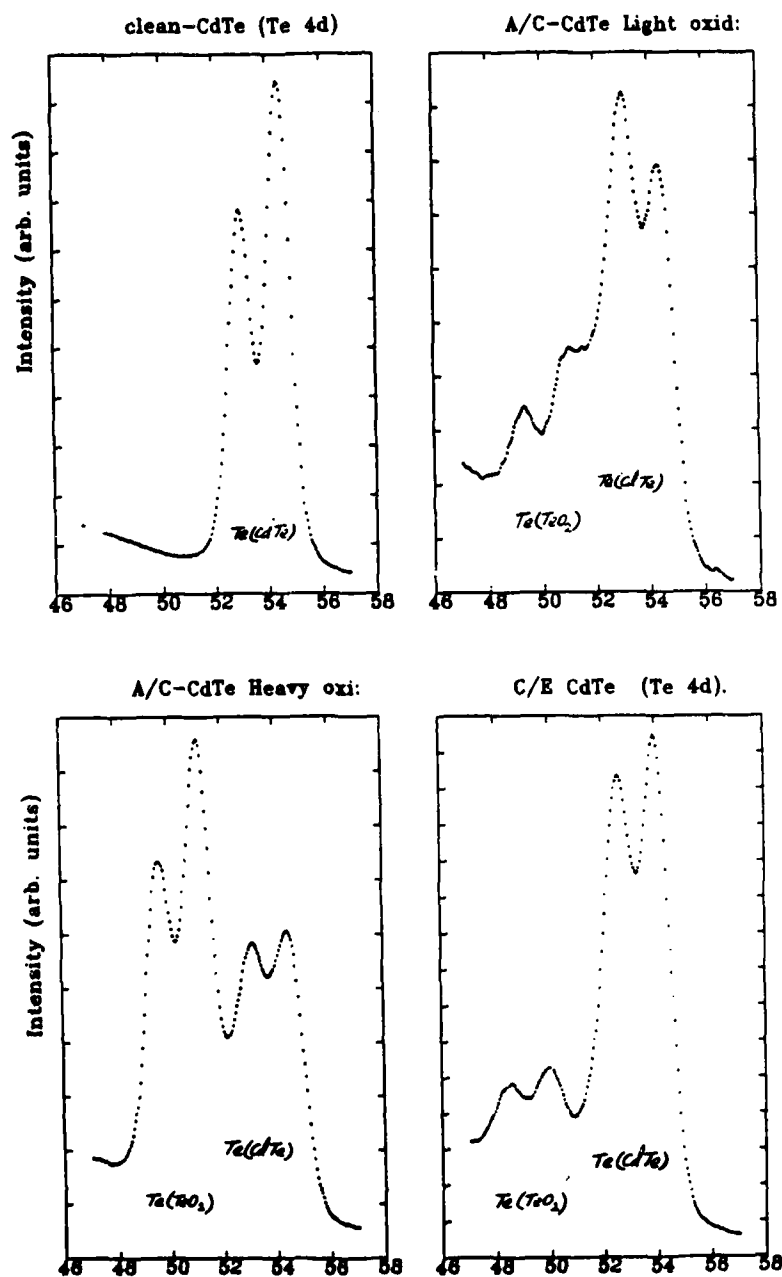


FIGURE 3. Soft x-ray photo-emission spectrum of Te 4d core level for (a) clean - cleaved (b) lightly oxidized (c) heavily oxidized and (d) bromine methanol etched CdTe surface. Photon energy is 100 eV.

In summary, these surface studies reveal that the vacuum cleaved surfaces are stoichiometric in Cd and Te, with no oxidation of the surface. Air-cleaved CdTe surfaces are stoichiometric in Cd and Te, but the bromine in methanol etched surfaces are slightly enriched in Te. These studies also show that both air-cleaved and bromine methanol etched surfaces have TeO_2 as a constituent of the surface layer. The thickness of the oxide layer varies in the range $(1 - 3)\text{\AA}$ depending on the degree of oxidation. The thickness of the Te-rich surface layer on chemically etched CdTe surfaces cannot be obtained from the results presented here alone. The estimated thickness of this Te-rich (Cd - deficient) layer using AES depth profiling is less than $\sim 10\text{\AA}$ (Feldman et al 1988) for the $\sim 1\%$ bromine in methanol treatment.

3.2 MICROSCOPIC INTERACTIONS OF METAL-CdTe INTERFACES.

Microscopic interactions at metal-CdTe interfaces were investigated by the more surface sensitive technique, SXPS using synchrotron radiation. Four metals were selected, namely Au, Ag, Cr and Mn for these studies. Au and Ag were chosen to represent the non-reactive noble metals and Cr and Mn to represent the most reactive metals. These studies were mainly carried out on clean and air-oxidized CdTe surfaces. Chemically etched CdTe surfaces have also been studied, but not for all four metals. CdTe surfaces were exposed to photons of 100 eV and photoexcited electrons were energy analysed using a double-pass cylindrical mirror analyser. Cd 4d, Te 4d core levels and valence band edges were monitored for the virgin surface and for the surfaces covered with varying amounts of metals.

(a) Ag, Au, Cr and Mn on clean surfaces.

Mn and Cr:

Figures 4 and 5 show the Te 4d, Cd 4d core levels and valence band spectra for clean CdTe surfaces as a function of Mn and Cr depositions respectively. First we consider the case of Mn(ref:6), and several spectral features can be clearly observed. At low coverages of Mn all spectral features of Te and Cd 4d shift to lower kinetic energy (higher binding energy) by about 0.3 eV, and they return back to its original position at higher coverages. A chemically shifted Cd 4d component appears ~0.9 eV towards the lower binding energy side at higher coverages of Mn. The position of this new component corresponds to the binding energy of metallic Cd and therefore this peak originates from dissociated Cd from CdTe. The fact that this peak is observed even at high coverages, which are much greater than electron escape depths (typically 3 to 7 Å), indicates the mixing of dissociated Cd with the Mn overlayer.

Attenuation rates for emission from the two semiconductor elements are different as shown in fig 6(a). The dotted lines show the ideal attenuation for escape depths of 4 and 5 Å. The Cd 4d emission undergoes a rapid attenuation while the Te 4d emission remains strong. The emission from the Te 4d core level drops to about 60% of its initial value and remains constant as the Mn coverage is increased.

Valence band features of CdTe are completely distorted and modified by the deposition of Mn on the CdTe surface, as shown in fig 4 indicating strong chemical reactions at the interface. The behaviour of Cr on clean CdTe is very similar to that of Mn on

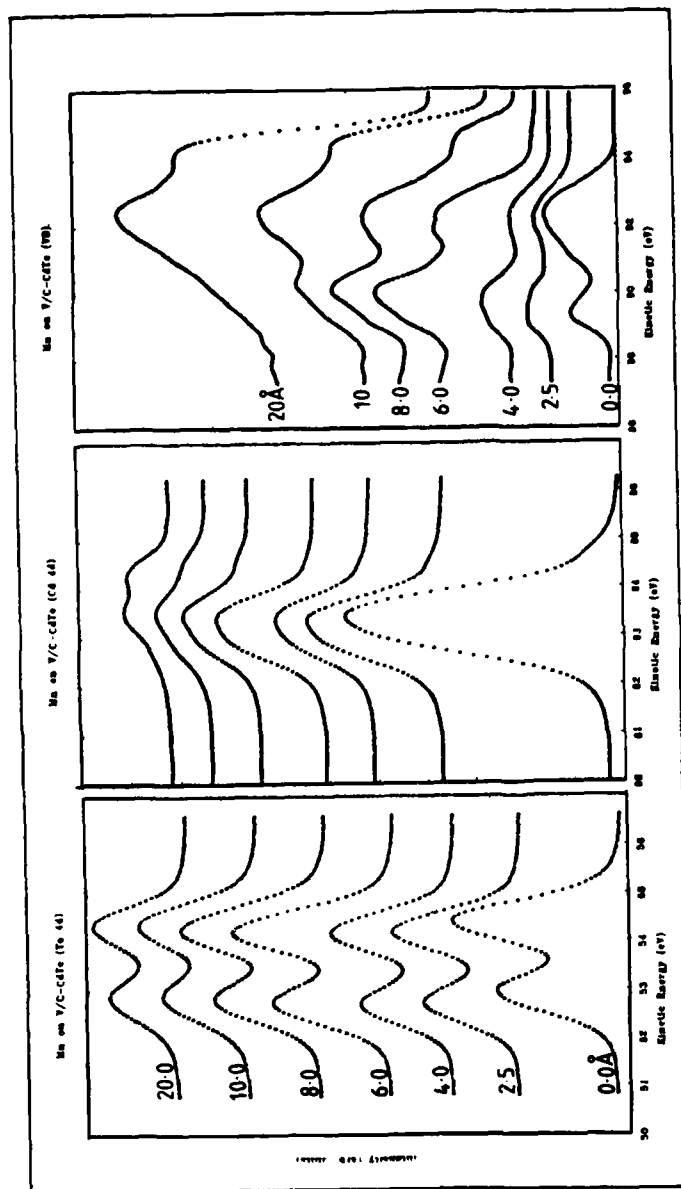


FIGURE 4. Te 4d & Cd 4d core levels and valence band spectra for clean CdTe surfaces as a function of Mn coverage. Spectra were taken at a photon energy of 100 eV and normalized to incident photon flux.

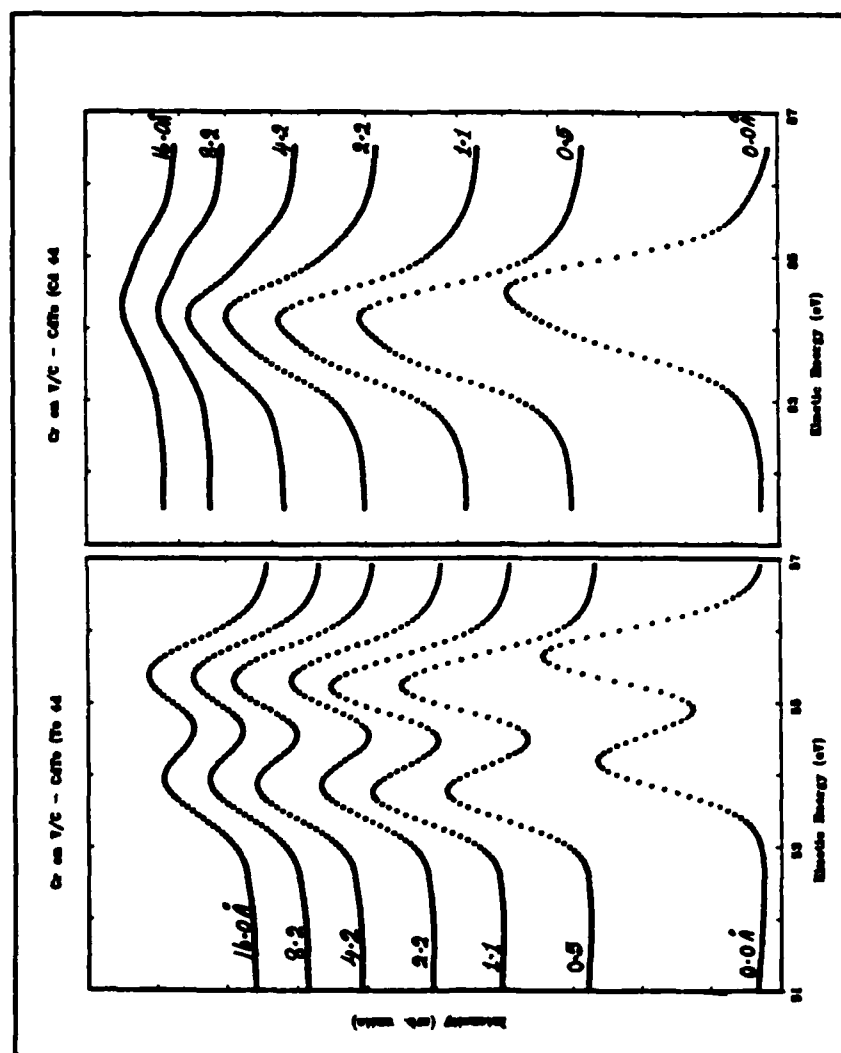


FIGURE 5. Soft x-ray photo-emission spectra of the Te 4d and Cd 4d core levels from clean CdTe surface with increasing coverages of Mn. Photon energy = 100 eV, and the spectra were normalized to incident photon flux.

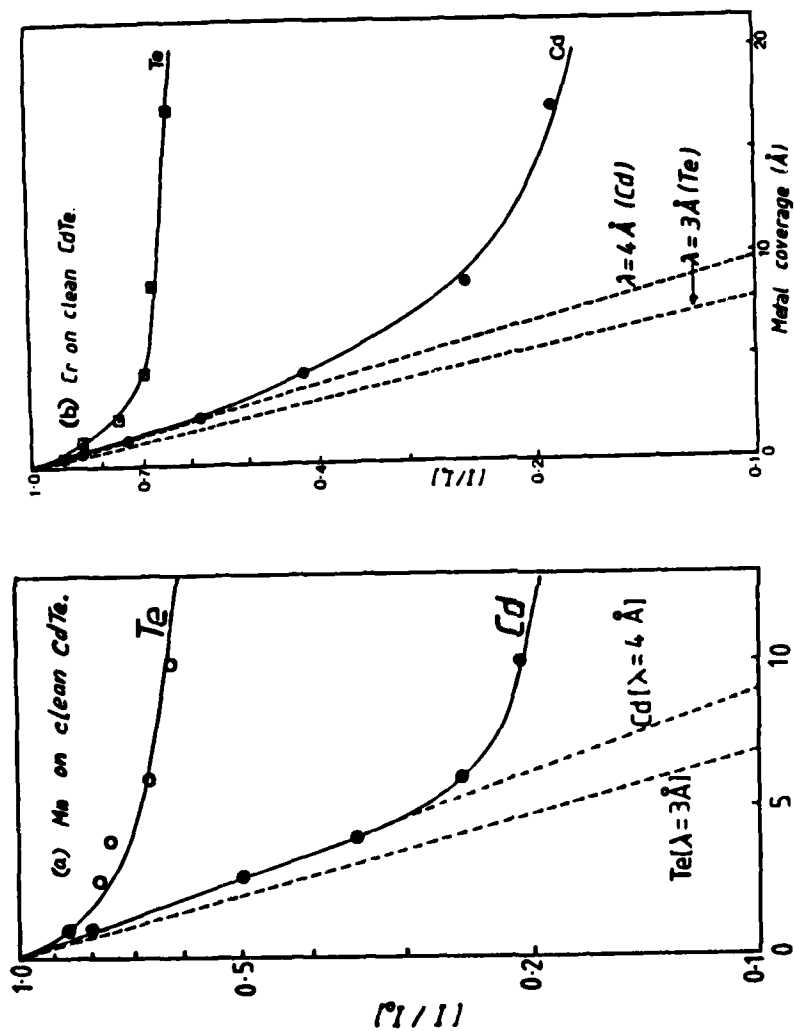


FIGURE 6. The attenuation of Te 4d and Cd 4d core level photoemission as a function of (a) Manganese, Mn (b) Chromium, Cr coverage.

CdTe as can be seen from fig 5 and 6(b). Therefore it is clear that both Mn and Cr, strongly react with CdTe surfaces to form their tellurides, releasing metallic Cd at the interface.

Au and Ag:

Fig 7 shows the Te 4d and Cd 4d core line spectra as a function of increasing Au coverage on the clean CdTe surface. The Cd 4d peak undergoes a gradual attenuation while the Te 4d emission remains strong as increasing amounts of Au are deposited. The normalized peak areas are plotted as a function of Au thickness on the surface, and are shown in fig 8. This clearly shows the different attenuation rates for the two semiconductor elements. Emission from Te 4d shows a saturation around 70% of that of the cleaved surface and remains at that level for increasing Au thickness.

The valence band spectra as a function of increasing Au coverage on the clean cleaved CdTe surface are shown in fig 9(a). Fig 9(b) represents the valence band spectrum of pure Au for comparison. This spectrum was obtained for thick layers of pure Au evaporated on a thin tantalum foil. All the spectra were obtained under the same conditions. The spin orbit splitting of 2.78 eV for pure Au reduces to 2.42 eV for Au layers on clean cleaved CdTe surfaces. These values agree well with XPS studies of Sham et al (1978) for bulk materials of pure Au and AuTe_2 . Comparison of these valence band spectra with their results suggest that the existence of other phases such as AuTe_2 in the top layers of Au metallization.

For the case of Ag on clean CdTe, the SXPS data are shown in fig 10. Chemical shifts associated with the Cd 4d emission are not observed for this case indicating the non-reactivity of Ag with CdTe. However, different attenuation rates for two semiconductor

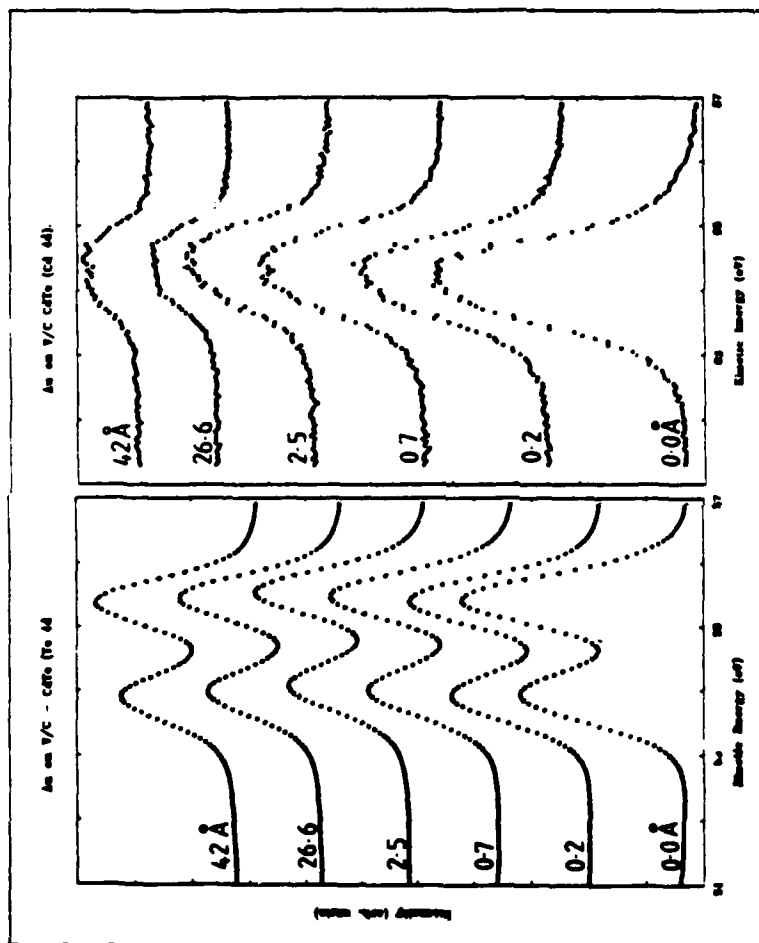


FIGURE 7. Soft x-ray photo-emission spectra of the Te 4d and Cd 4d core levels from clean CdTe surface with increasing coverages of Au. Photon energy = 100 eV, and the spectra were normalized to incident photon flux.

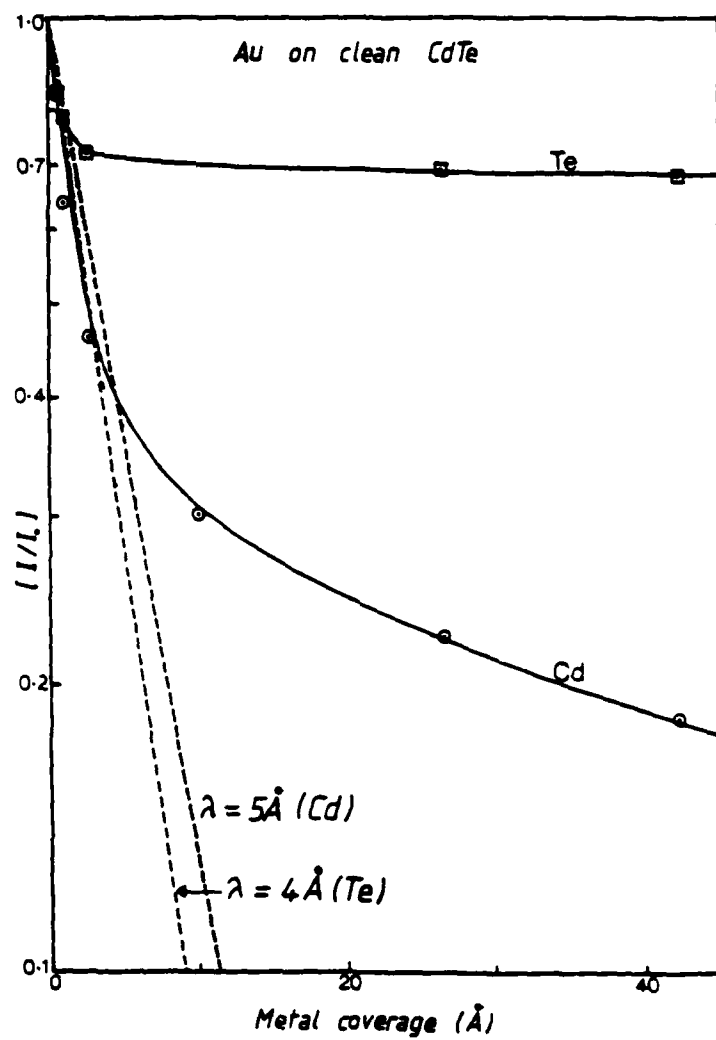


FIGURE 8. The attenuation of Te 4d and Cd 4d core level photoemission as a function of Gold, Au, coverage.

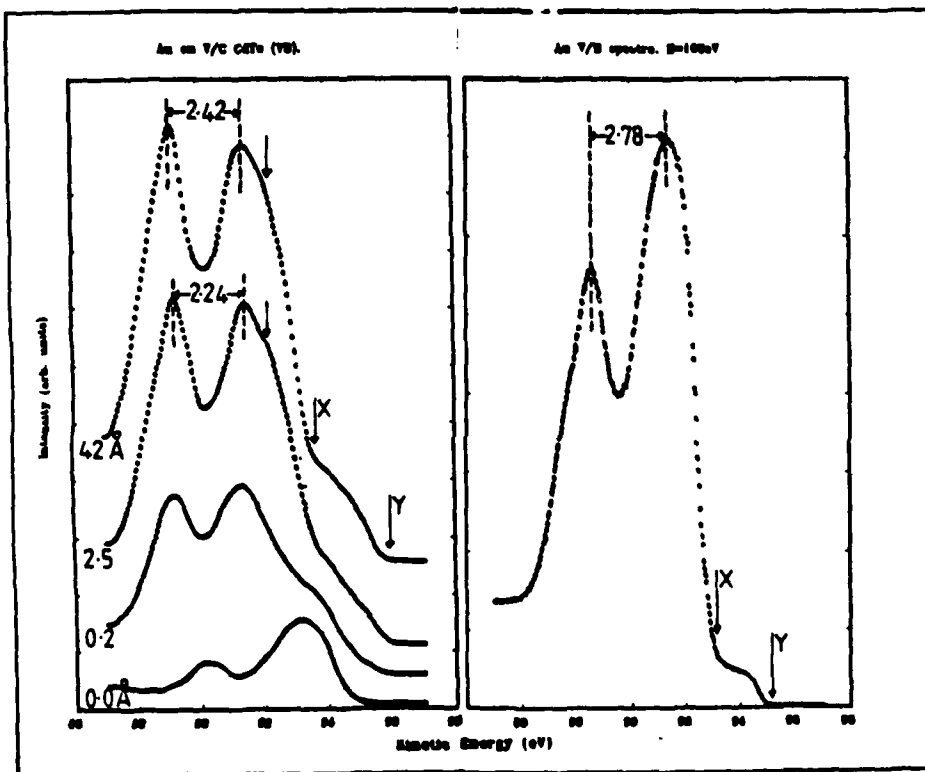


FIGURE 9. (a) The valence band spectra as a function of increasing Au coverage on clean cleaved CdTe. The spectrum shown in (b) is for a thick layer of pure Au deposited on a tantalum foil. All the spectra were taken at photon energy of 100 eV.

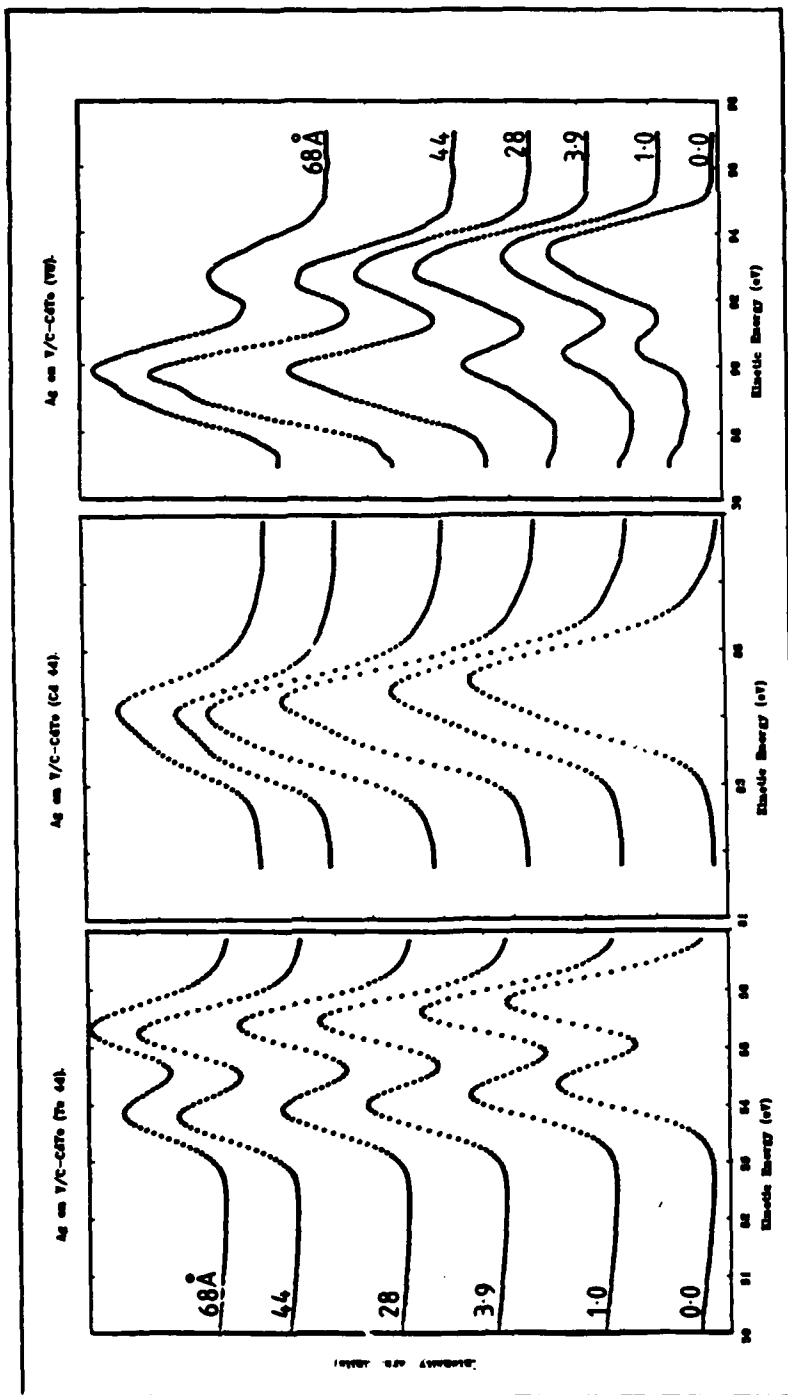


FIGURE 10. Te 4d & Cd 4d core levels and valence band spectra for clean CdTe surfaces as a function of Ag coverage. Spectra were taken at a photon energy of 100 eV and normalized to incident photon flux.

elements (see fig 11) indicates a strong out-diffusion of Te at the Ag/CdTe interface similar to Au/CdTe system.

(b) Ag, Au, Cr and Mn on air-cleaved surfaces.

Mn and Cr:

Fig 12 shows the SXPS data for Mn on the heavily oxidized CdTe surface (ref:3). The spin orbit split Te $4d_{5/2}$ and Te $4d_{3/2}$ emission for the oxidized surface also has an additional doublet at ~ 3.4 eV to higher binding energy. This emission originates from tellurium atoms in TeO_2 on the CdTe surface. Deposition of Mn onto these surfaces lead to dramatic changes in the SXPS spectra. The Cd 4d emission is attenuated quite rapidly, similar to that of Mn on clean CdTe surface. However, the Te 4d emission is influenced in a completely different way. Firstly, the TeO_2 component is reduced and ultimately removed and at the same time the emission of unoxidized tellurium increases. Clearly this is due to a reduction of tellurium oxide. For larger Mn coverages there is a slow reduction of the Te 4d emission intensity as the Mn overlayer attenuates substrate emission. Fig 13 shows similar data for Cr on air-oxidized CdTe surface(ref:4). These results indicate that the behaviour of Cr is very similar to that of Mn, and their behaviour agrees well with the thermodynamic predictions.

Ag and Au:

The SXPS spectra obtained for Ag and Au on air oxidized CdTe surfaces are shown in figures 14 and 15 respectively. In the case of Ag, Cd 4d emission and $Te(TeO_2)$ emission show a gradual attenuation. Reduction of TeO_2 is not observed in this case in accord with the bulk thermodynamic data(ref:8). The emission from

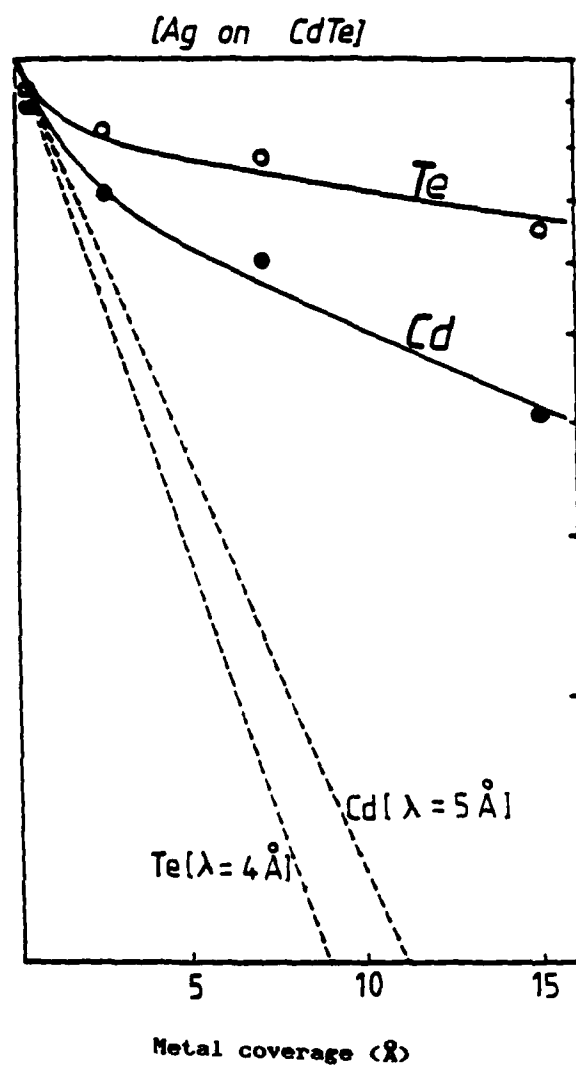


FIGURE 11. The attenuation of Te 4d and Cd 4d core level photoemission as a function of Silver, Ag coverage.

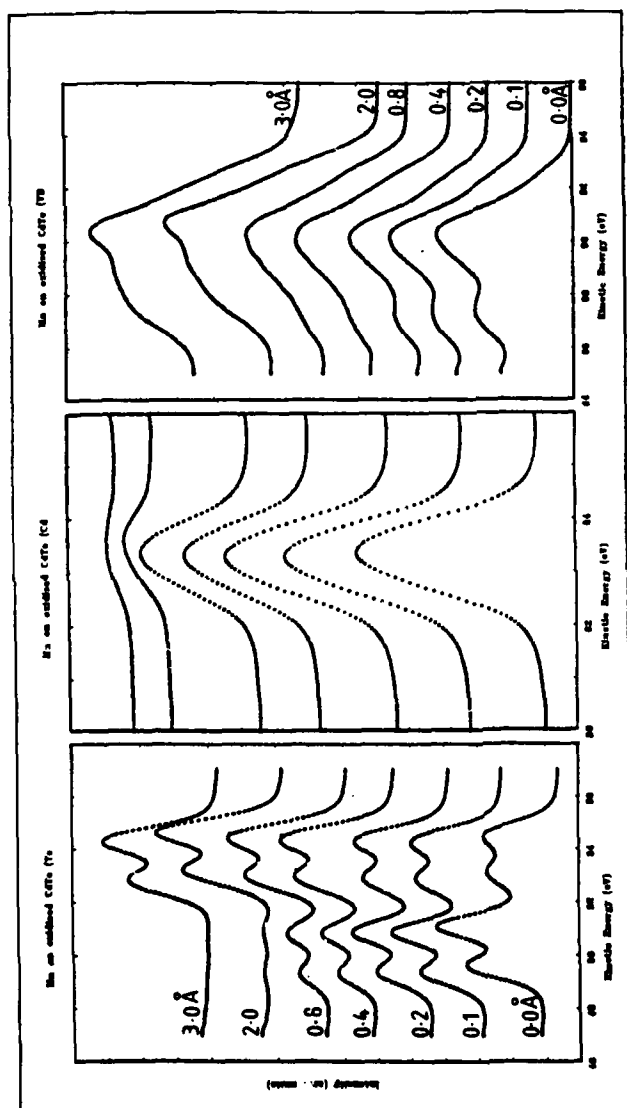


FIGURE 12. Te 4d & Cd 4d core levels and valence band spectra for oxidized CdTe surfaces as a function of Mn coverage. Spectra were taken at a photon energy of 100 eV and normalized to incident photon flux.

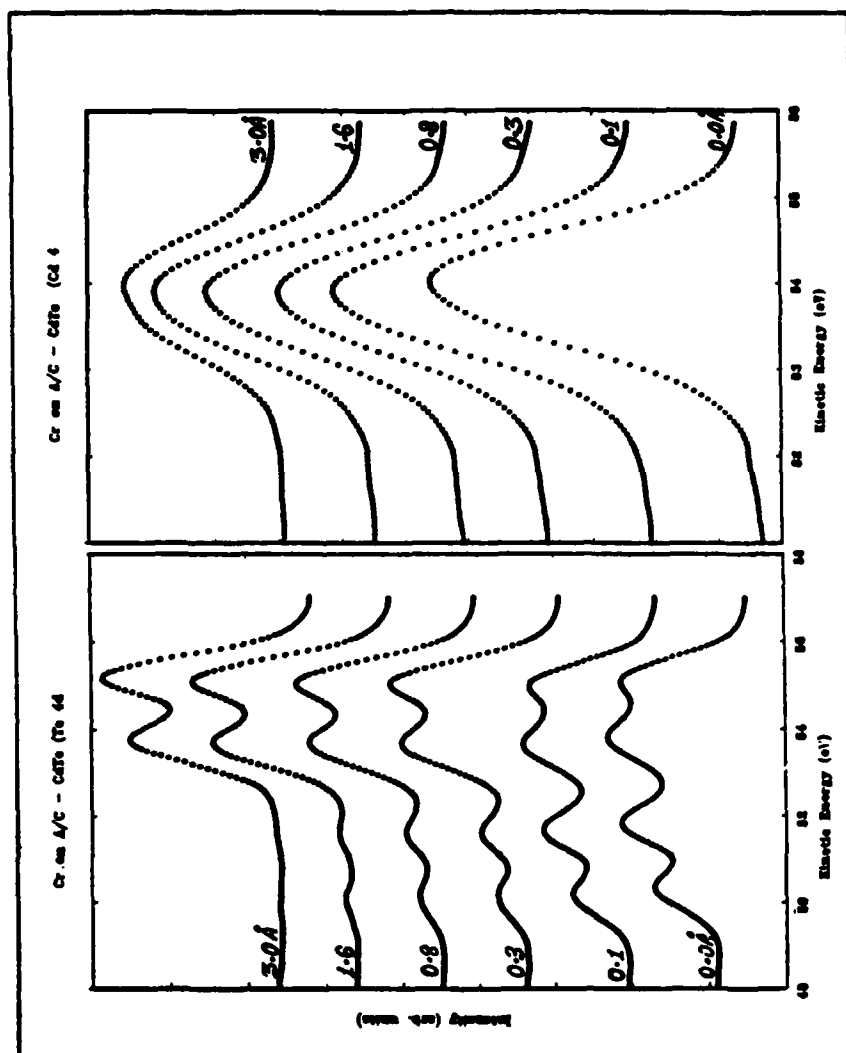


FIGURE 13. Soft x-ray photo-emission spectra of the Te 4d and Cr 4d core levels from oxidized CdTe surface with increasing coverage of Cr. Photon energy = 100 eV, and the spectra were normalized to incident photon flux.

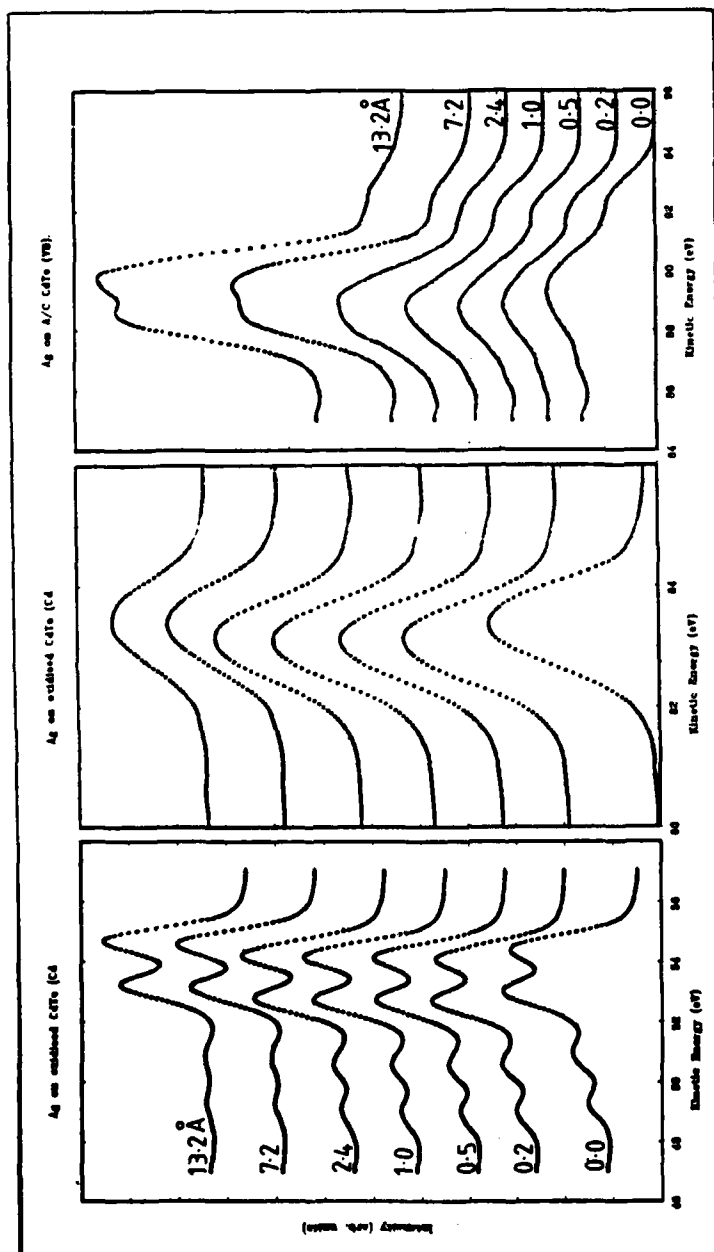


FIGURE 14. Te 4d & Cd 4d core levels and valence band spectra for oxidized CdTe surfaces as a function of Ag coverage. Spectra were taken at a photon energy of 100 eV and normalized to incident photon flux.

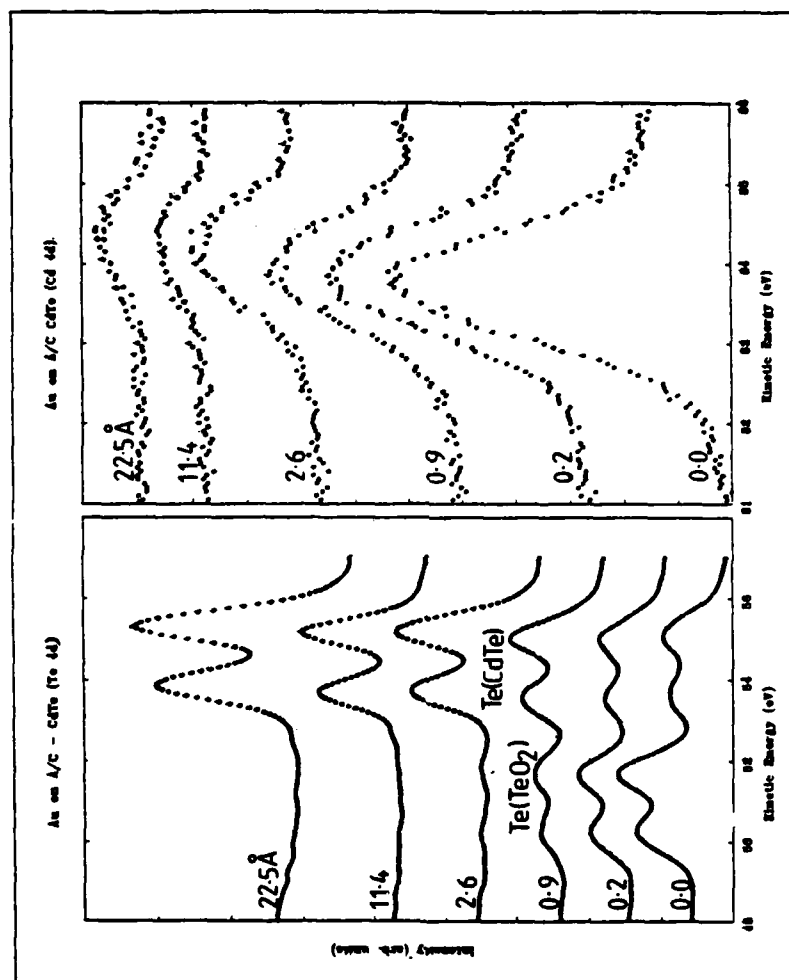


FIGURE 15. Soft x-ray photo-emission spectra of the Te 4d and Cd 4d core levels from oxidized CdTe surface with increasing coverages of Au. Photon energy = 100 eV, and the spectra were normalized to incident photon flux.

Te 4d remains strong with increasing Ag coverage, as observed for clean surfaces. Au on oxidised surfaces, however, shows a complicated behaviour (see fig 15). Deposition of very thin layers of Au on the oxidized CdTe surface leads to an attenuation of the Cd 4d emission as expected. But the component associated with TeO_2 is rapidly attenuated and the lower binding energy component $\text{Te}(\text{CdTe})$ increases continuously in intensity at least up to 22 Å. Although the attenuation of TeO_2 is very similar to the cases of Mn & Cr, the reduction of TeO_2 by Au is quite unexpected on thermodynamic grounds. The alternative explanation for the observed rapid attenuation of the $\text{Te}(\text{TeO}_2)$ component is the escape of oxygen from TeO_2 during Au deposition which is unlikely, or a rapid burying of oxide due to growth of an overlayer consisting of Au, AuTe_2 & Te. For this reason the emission from Te 4d remains strong even at higher coverages of Au.

(c) Mn on bromine methanol etched surfaces.

Fig 16 shows the SXPS spectra corresponding to the Te 4d and Cd 4d core level emission for the etched CdTe surface and following deposition of increasing amounts of Mn. The detailed results of this system are presented and discussed in (ref:5). These investigations clearly show that complex microscopic interactions occur between the Mn and the chemically etched CdTe surface. Mn interacts with CdTe to form manganese telluride and/or cadmium manganese telluride, releasing metallic Cd at the interface. Mn also reduces the surface TeO_2 , forming manganese oxide and manganese telluride.

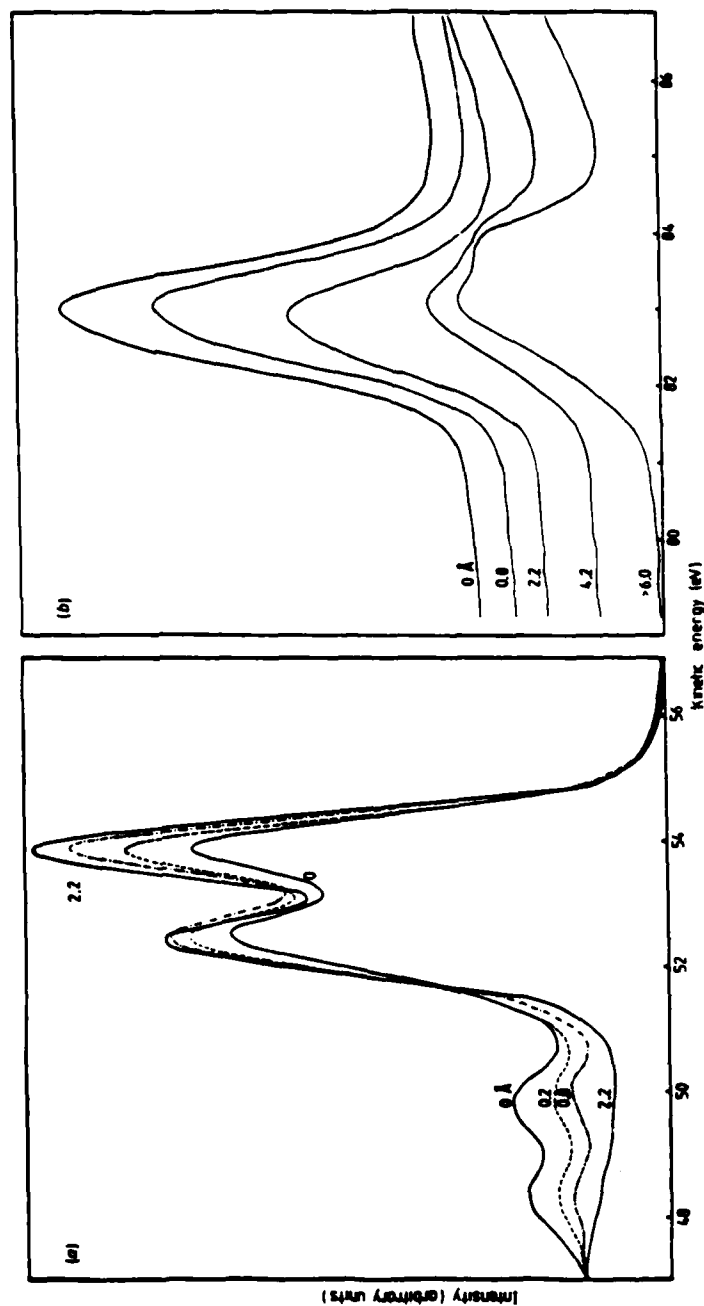


Figure 15. Soft x-ray photo-emission spectra of (a) Te 4d and (b) Cd 4d core levels measured from a chemically etched CdTe surface with increasing coverages of Mn (shown on the curves in A). Spectra were taken at a photon energy of 100 eV and normalised to incident photon flux.

(d) AES studies on Au-CdTe (1% bromine meth: etched) interfaces.

Fig 17 shows the AES spectra recorded for a chemically etched CdTe surface, and the same surface covered with $\sim 40 \text{ \AA}$ of Au. For the chemically etched surface, a large C peak is observed, and the Cd and Te peaks are approximately equal in height. The ratio of peak heights of Te and Cd (h_{Te}/h_{Cd}) for this surface is 1.0. Deposition of Au on this surface shows different attenuation rates for the two semiconductor elements. The relative intensity of the Te peak increases with the higher coverages of Au. For the surface covered with $\sim 40 \text{ \AA}$ of Au, the above peak height ratio is ~ 2.0 , and this clearly indicates the strong preferential out-diffusion of Te at the interface. The emission from Cd, even at thick coverages (40 \AA) of Au suggests the intermixing of Cd with the Au overlayer. Attenuation of the oxygen peak is also clearly shown in these spectra. Therefore the AES technique also confirms the strong out-diffusion of Te and intermixing of Au and Cd at the interface.

3.3 MACROSCOPIC STUDIES OF METAL-CdTe INTERFACES.

Transport properties of metal-CdTe contacts were studied using conventional I-V and C-V methods. Detailed I-V and C-V characteristics for some of the contacts studied have already been published (ref: 1, 2 & 5). Forward current-voltage characteristics have been analysed using thermionic emission theory in order to evaluate the barrier heights. Great care was taken to correct for generation recombination currents (ref: 2). For certain cases, values of low barriers were obtained by photoelectron spectroscopy. In fig 18 we present the measured Schottky barrier heights for metals on clean, bromine methanol etched and air-cleaved n-CdTe single crystals. Several important points may be made.

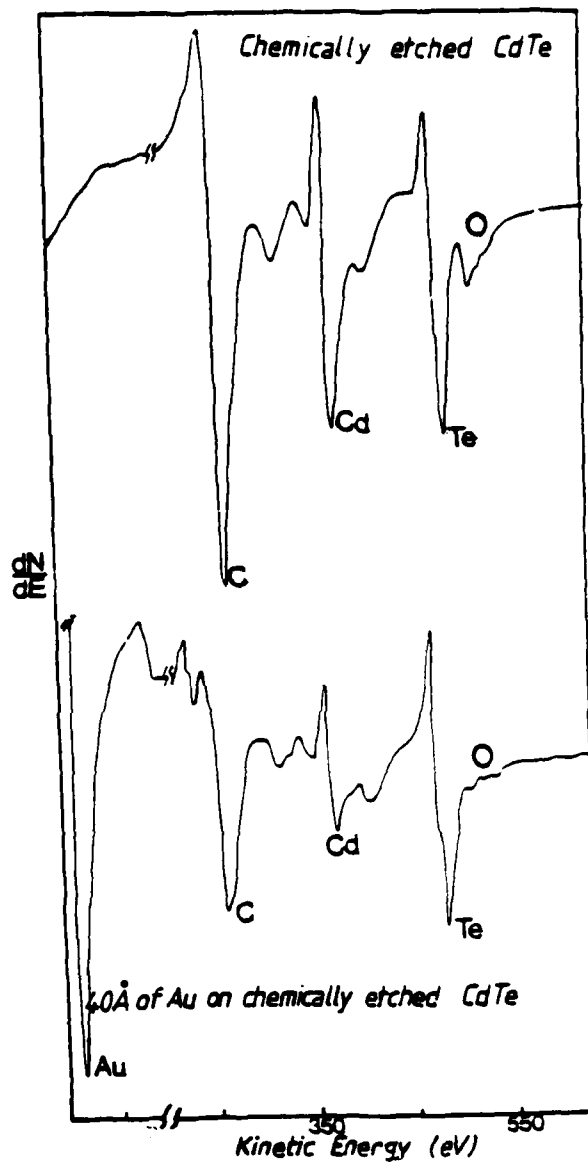


FIGURE 17. Auger spectra for chemically etched CdTe and 40 Å of Au on that surface. Note the increase in Te signal due to strong out-diffusion of this element.

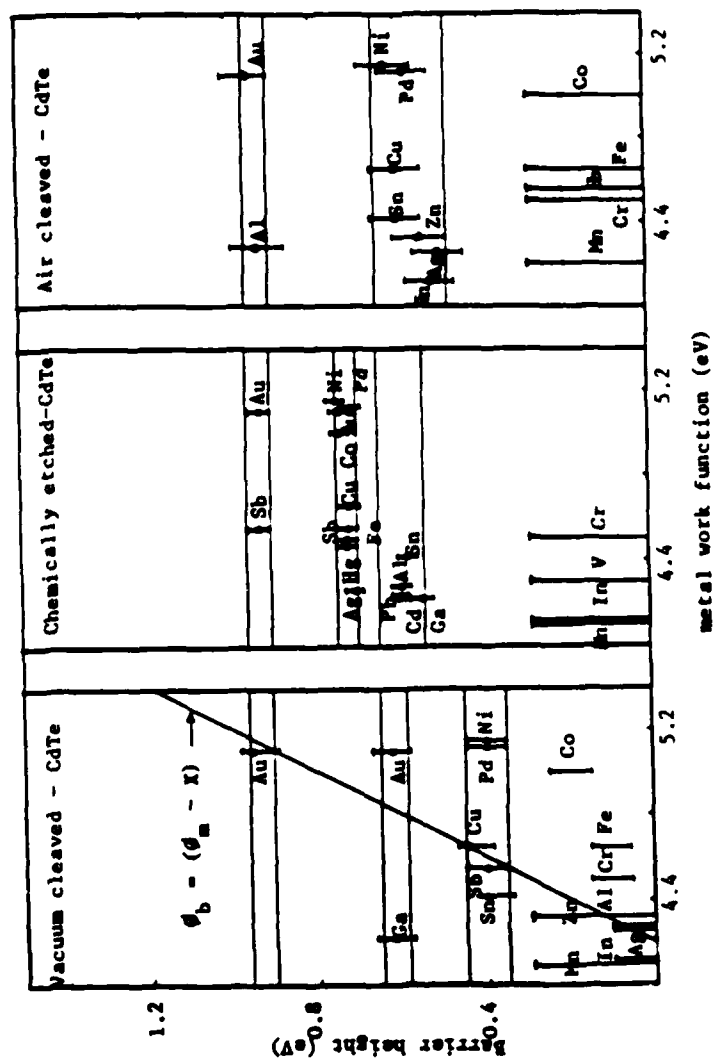


FIGURE 18. Plot of Schottky barrier heights against metal work functions for metals on (a) clean - cleaved (b) chemically etched and (c) air - cleaved n-CdTe single crystals.

(a) Metals on clean CdTe surfaces(ref:4).

I. Metals on clean surfaces give rise to a range of values of barrier heights, varying from close to zero to 0.9 eV as shown in fig 18(a).

II. Au consistently appears to yield values of ϕ_b close to 0.9 eV or close to 0.6 eV on clean surfaces.

III. Clearly, the data presented in fig 18(a) is not consistent with the elementary model of Schottky, where a linear dependence of ϕ_b on ϕ_m is expected.

IV. The data is also quite inconsistent with models involving pinning of the Fermi level by metal induced gap states, or MIGS. Clearly, the existence of two distinct values for the barrier height cannot be explained from this model.

(b) Metals on 1% bromine methanol etched-CdTe surfaces(ref:5).

I. Metals on etched surfaces yield completely different barriers to those obtained for clean surfaces. Most metals yield a constant barrier of 0.72 ± 0.03 eV.

II. More reactive and low work function metals tend to yield lower barriers or ohmic contacts.

III. The two valued barrier heights (0.72 eV or 0.93 eV) are also found with Au and Sb on these surfaces.

(c) Metals on air-cleaved CdTe surfaces(ref:4).

The barriers on air-cleaved CdTe surfaces are less reproducible, and fall into 3 main groups; metals producing low barriers(Cr, Mn, ...), intermediate barriers(Ni, Pd, Cu, Sn, Zn, ...) and high barriers(Au, Al, ...).

Experimentally observed Schottky barrier heights suggests that the existence of interfacial defect levels for the three different surfaces studied. Clearly a level at 0.92 ± 0.03 eV is found for all surfaces depending on their surface conditions. The pinning at 0.72 ± 0.03 eV for chemically etched CdTe is due to the states created by Te-rich (Cd-deficient) surface layer(ref:5). The metals Mn, V, and Cr yield very low barriers for both clean and oxidised surfaces.

(d) Ageing of metal-CdTe contacts.

Ageing of high barrier contacts made on bromine in methanol etched CdTe surfaces show large variations in transport properties with time. The forward current of "as made" diodes has a considerable contribution from recombination and generation at the depletion region. This is shown by curve (A) in fig 19. The recombination current contribution reduces gradually and therefore the ideality factor improves with time (curve B), when the diodes are stored under normal atmospheric conditions. In table 2 we show the variation of some important parameters for a similar diode. The n-factor decreases from 1.26 to 1.09 and the recombination current reduces by over one order of magnitude within approximately 10 weeks after fabrication. This shows that the interactions at the interface continue with time even at room temperature and help to remove recombination centres present at the interface and to improve the rectification properties of the diode. It is also evident that these centres are mainly located at the vicinity of the metal contact, and not in the depletion layer far away from the contact.

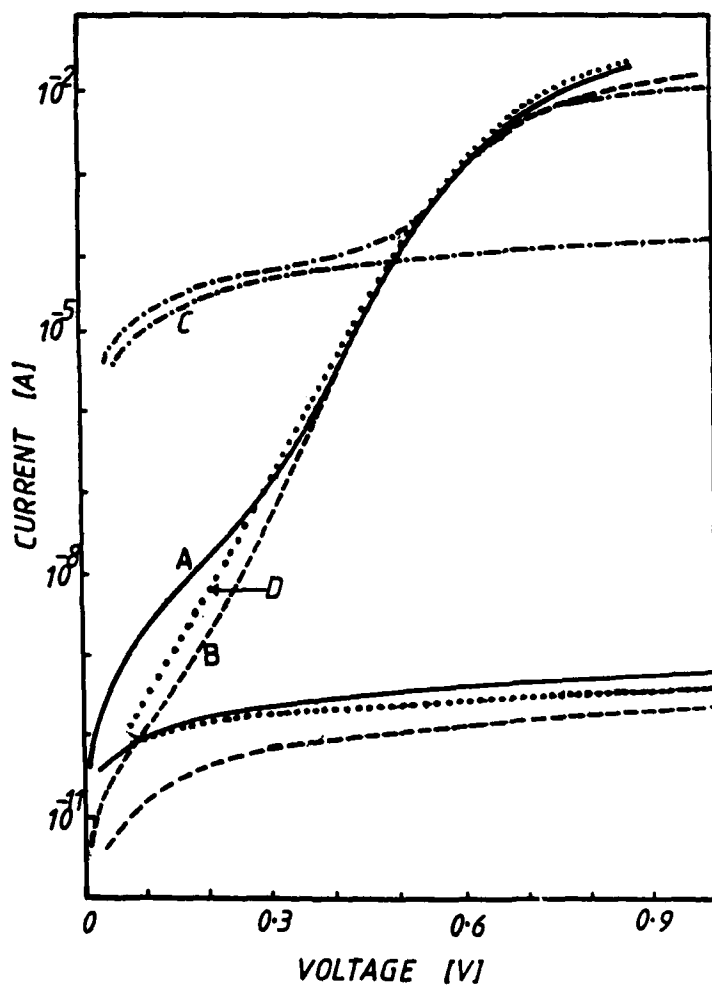


FIGURE 19. Effects of ageing on electrical properties of Au/CdTe(chemically etched) Schottky diodes. curve (A) represents the I-V for "as made" diode, curve (b) after ~10 weeks exposure to atmosphere, curve (c) after 8 months and curve (d) after isolation of diodes by chemical etching.

TABLE 2.
variation of some parameters of Au/CdTe diodes with time

Age(weeks)	n	Recombination current (A)
0	1.26	2.0×10^{-10}
2	1.19	5.0×10^{-11}
4	1.16	3.0×10^{-11}
10	1.09	2.0×10^{-11}

If these diodes are left in air for a few months, the rectification property disappear gradually as shown by curve (C) in fig 19. It is apparent that the high currents at low voltages are ohmic and the diode properties are completely masked by this ohmic current. This current contribution can arise due to three main reasons: surface leakage, the additional conduction due to changes at the periphery of the contact or the high currents due to field emission via the spikes formed at the interface. Isolation of diodes by simply scribing narrow groves around metal contacts recovers the rectification property again. This procedure changes the (I-V) characteristics from curve (C) to curve (D) as shown in fig 19. This observation clearly confirms that the ohmic current contribution is mainly due to the surface leakage. The Te-rich surface layer left by bromine methanol etch can easily provide a parallel conduction path (Montgomery 1964) with the diode. This is however not observed for "as made" diodes. It may be possible to form a more conducting surface layer on chemically etched CdTe crystals with time, when exposed to normal atmospheric conditions.

(e) Thermal stability of metal-CdTe contacts.

The effects of thermal annealing on electrical properties of metal-CdTe contacts were also studied in detail. The high barrier (0.93 eV) contacts produced with three metals (Ag, Sb, Au) were selected. Annealing of the thick metal contacts was performed in a vacuum of $\sim 10^{-6}$ Torr for 20 min each at different temperatures. The I-V measurements were performed in atmospheric conditions at room temperature.

SILVER(Ag):

Ag on chemically etched CdTe surfaces forms two sets of diodes with two values for the barrier heights(0.72 eV and 0.93 eV). Typical I-V characteristics are shown by the two curves labelled (a) in fig 20. Annealing at 100°C for 20 min, completely removes the rectification properties and shows a good ohmic behaviour. These curves are shown by the two curves labelled (b) and they are controlled by the bulk resistance of the material ($\sim 4 \Omega$).

ANTIMONY(Sb):

Sb on CdTe surfaces produces the most stable and noise free contacts. A typical Schottky diode with a high barrier (0.93 eV) is shown in fig 21, and stays unchanged when annealed at 300°C for 20 min. However, annealing at 400°C for 20 min completely reduces the rectification property (solid curve in fig 21) and introduce a very large series resistance to the contact. Although the bulk material introduces only a few ohms to the series resistance this shows a resistance in the M Ω region. This

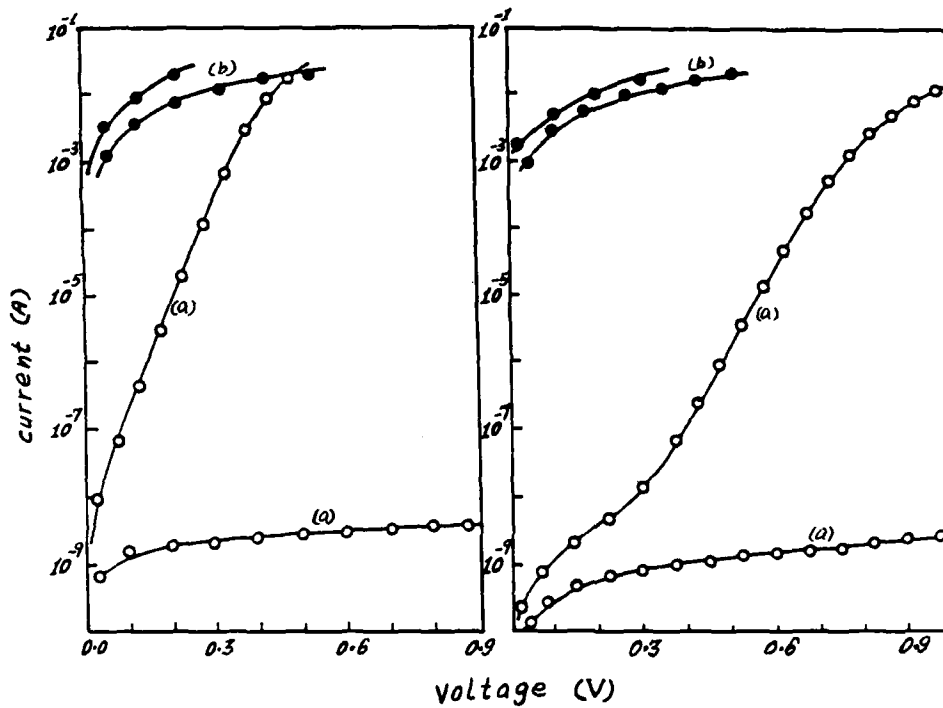


FIGURE 20. (I-V) characteristics of two sets of diodes (barrier heights 0.72 & 0.93 eV) obtained with Ag on chemically etched CdTe surfaces. (o) the characteristics for "as made" diodes and (•) the characteristics after annealing at 100°C for 20 min.

indicates a formation of a semi-insulating layer at the vicinity of the metal contact due to doping of n-CdTe crystal. Sb is a p-type dopant in CdTe and therefore compensation can occur at the interface due to diffusion of Sb atoms at high temperatures. These acceptors compensate the donors and produces a highly insulating layer at the interface. This resistance is clearly shown in the series resistance of the diode.

GOLD(Au):

The annealing effects of Au/n-CdTe high barriers (see fig 22) show interesting results. Annealing at 75°C for 20 min reduces the barrier height from 0.93 to 0.72 eV. Consequent annealings up to 225°C for 20 min, does not change this barrier height, but above 300°C contacts become ohmic.

The annealing effects of Ag and Au contacts to CdTe indicate a rapid removal of interface states responsible for Fermi-level pinning at 0.93 eV. However, the use of Sb increases the thermal stability of the contact most probably due to p-type doping of the semiconductor, CdTe. These contacts withstand the annealing at 300°C for 20 min and retain their good rectification properties.

4.0 CONCLUSIONS

Surface analysis by ESCA, AES and SXPS show that the bromine methanol etched CdTe surfaces are not stoichiometric in Cd and Te, but slightly enriched in Te. The thickness of this layer is ~10 Å (Feldman et al 1985) for the case of 1% bromine in methanol treatment. A very thin layer, of (~1-2 Å thick) TeO₂ also exists on this Te-enriched layer.

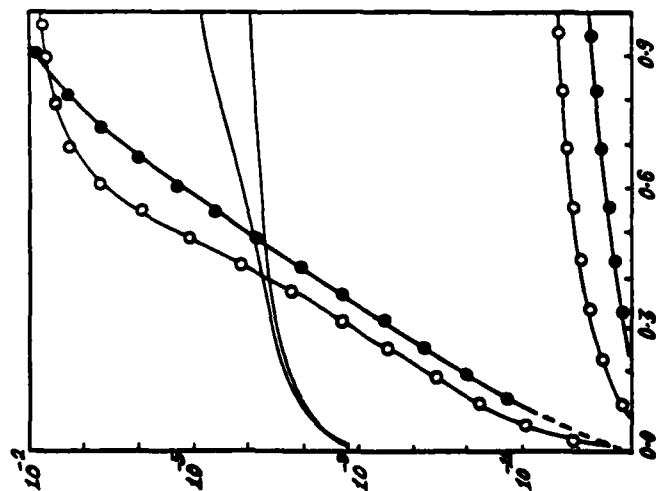


FIGURE 21. I-V characteristics of Sb/n-CdTe diodes measured at room temperature.
 (o) "as made" diode.
 (●) Annealed at 300°C for 20 min.
 — Annealed at 400°C for 20 min.

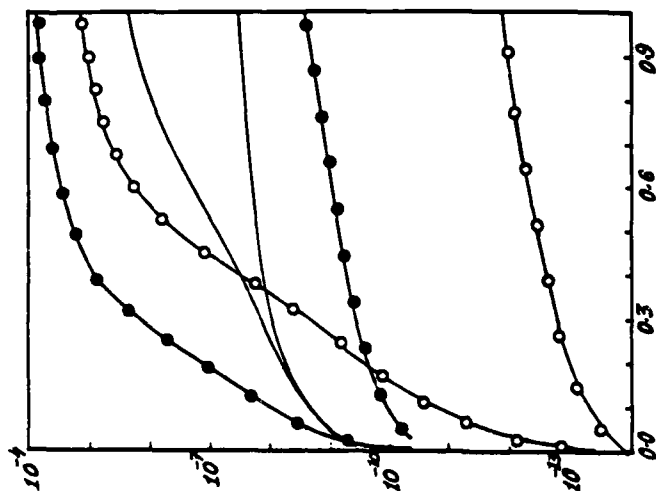


FIGURE 22. I-V characteristics of Au/CdTe diodes, measured at room temperature.
 (o) "as made" diode.
 (●) Annealings at temperatures between 78°C and 225°C.
 — Annealed at 300°C for 20 min.

Air-oxidized CdTe surfaces also consists of a thin layer of TeO_2 , depending on the degree of oxidation. Heating the surfaces in air produces a $\sim(3 - 4)\text{\AA}$ thick layer of TeO_2 . The presence of any other possible oxides has not been observed from the results presented in this report.

SXPS studies confirm that a few different kinds of interactions take place at the metal-CdTe interfaces. Most of the metals react with CdTe, to form more stable metal tellurides or/and metal cadmium telluride, releasing Cd at the interface. These reactions can be well predicted using bulk thermodynamic data for most of the metal-CdTe systems studied(ref:5).

In all cases, a strong out-diffusion of Te is observed. Especially the two metals Au and Ag show this interaction clearly, and similar results have been observed for Cu on CdTe (Friedman et al 1986). We suggest that this is due to the formation of metal/Cd alloy at the interface. The Te, released from CdTe diffuses outward, and form a layer consisting of Te and metal telluride on top of the metal contact. Alloying of Au and Ag with Cd should be very strong according to thermodynamical data(ref 5) and indeed our observations agree with these predictions. Intermixing of Cd with metal is also clearly observed from data presented in this report.

In the case of the oxidized surface, the evaporated metal reacts with the native oxide TeO_2 , forming metal oxide and metal telluride at the interface. These oxide layers do not act as a reaction or diffusion barrier between the metal and the semiconductor. Bulk thermodynamic data again predicts these reactions (ref:5) for most cases except Au. Ag is the only metal that shows an inert behaviour on this native oxide layer.

Transport studies on metal-CdTe contacts show that good ohmic or Schottky barrier contacts can be made very easily on n-CdTe single crystals. Electrical barriers up to 0.93 eV can be achieved, and they exhibit excellent rectification ratios, upto 10^{11} in certain cases. Sb provides the most noise free and most reliable contacts to n-CdTe single crystals. In most cases I-V characteristics can be well described by thermionic emission theory combined with the recombination & generation in the depletion layer. Recombination centres at the interface arise mainly from bulk defects or imperfections created during chemical etching and device fabrication.

The mechanism of formation of Schottky barriers at metal-CdTe interfaces cannot be explained in terms of the simple Schottky or metal induced gap states (MIGS) models. The observation of two distinct barrier heights for Au, Sb and Ag strongly suggests the pinning of the Fermi level at different defect levels. CdTe surface treatments prior to metal evaporations or the strong chemical reactions during metal evaporation can create these defects at the vicinity of the metal contact.

Ageing of high barrier metal-contacts tends to remove the recombination centres, via continuous interactions occurring at the interface. This improves the rectification property of the contact. However, the exposure to normal atmospheric conditions can increase surface leakage and mask the rectification behaviour completely. Most of the contacts lose their rectification properties with annealing over 250°C. The best thermal stability was with Sb, and these diodes withstand annealing at 300°C.

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METAL CONTACTS TO SEMICONDUCTORS, INDIUM PHOSPHIDE AND CADMIUM TELLURIDE

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The Schottky barriers formed by a range of metals on InP(110) and CdTe(110) surfaces have been studied by a range of methods, concentrating in particular on Ga overlayers on InP, and Sb, Pd, Co, Cr and Fe on CdTe. Substantial differences are observed depending on whether the semiconductor surface is chemically etched, cleaved in air, or cleaved in vacuum. These differences are largely consistent with previous studies and are discussed in terms of the various models available to describe Schottky barrier formation.

1. Introduction

During the last ten years our understanding of the nature of metal-semiconductor interfaces has improved considerably as a result of the application of modern surface science techniques in association with conventional studies such as transport across the interfaces. Techniques such as Auger electron and soft X-ray photoelectron spectroscopies have shown that intimate interfaces formed between many metals and semiconductors are not ordered and abrupt with chemical reactions and interdiffusion across the boundary being commonly observed [1-3]. Attempts are under way in many laboratories to understand processes at metal-semiconductor interfaces in terms of thermodynamic and chemical considerations. Central to most studies is the desire to understand those processes which control the formation of Schottky barriers. The early theories of Schottky [4] and Bardeen [5] have been extended more recently to include the influence of defects at the interface [5-7] and also to consider metal-induced gap states (MIGS) arising from the penetration of the metal wavefunctions into the semiconductor [6-8]. Recently Tersoff [9,10] has discussed the latter model in some detail and has shown that simple

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considerations of local charge neutrality near the metal–semiconductor interface suggests that the Fermi level at the interface will be pinned near an effective gap centre which is simply related to the bulk semiconductor band structure. This theory appears to give good agreement with the pinning energies of several metal–semiconductor systems and has also been applied successfully to account for the magnitude of band offsets at semiconductor heterojunctions.

The most thoroughly studied systems experimentally are metals on Si and on GaAs. Schottky barriers on n-Si appear to be in the range 0.4–0.9 eV with the majority of metals yielding barriers in the range 0.6–0.7 eV [11]. Most metals on n-GaAs yield barriers in the range 0.75–0.9 eV showing a remarkable degree of independence to the nature of the metal. Attempts have been made to understand Schottky barriers on III–V solids in terms of the Tersoff model [9,10] and the defect model [5,12,13] but at the present time the prime cause of Fermi-level pinning in these or other systems is not fully understood. Clearly detailed studies of a wider range of metal–semiconductor systems are required together with experimental tests designed to investigate the validity of the various theories and models proposed. In this paper we describe studies of this kind aimed to examine the validity of metal-induced gap states as the prime reason for Fermi-level pinning and Schottky barrier formation.

In the present studies we have examined further the nature of metal contacts to InP and CdTe cleaved surfaces. Both of these have band gaps and effective masses close to those of GaAs so that the influence of wavefunctions tunnelling from the metal should be similar for GaAs, InP and CdTe. On the basis of the Tersoff model [9,10] in its simplest form, therefore, one may anticipate Schottky barriers on InP and CdTe which are independent of the metal as appears to be the case for GaAs. Also, separation of the metal and semiconductor by an intervening interfacial layer, e.g., an insulating oxide, may also be expected to influence charge spillage from the metal into the semiconductor and thus Schottky barrier formation. Indeed, this seems to be the case for the metal–SiO₂–Si system [11]. In these studies we consider also the influence of intermediate layers at metal–CdTe and metal–InP interfaces.

2. Experimental

The studies described involved the application of a range of experimental techniques including low-energy electron diffraction, Auger electron spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. They also include studies of the electrical properties of the interfaces by current–voltage and capacitance–voltage methods. The InP crystals used were provided by MCP, Ltd., with carrier density $\approx 5 \times 10^{15} \text{ cm}^{-3}$. The

n-type CdTe crystals were grown in our laboratories and had carrier density $\approx 10^{16} \text{ cm}^{-3}$. Crystals obtained commercially were also used but were found to be of inferior quality, giving very poor Schottky diodes; for this reason no results using these will be reported. Further details of our experimental techniques have been published elsewhere [14,15].

3. Results

3.1 Metals on indium phosphide

The Schottky barriers formed by a range of metals on n- and p-type InP crystals have been studied by numerous groups [2, 14–20]. The measured barriers in practically all cases correspond to pinning energies in the upper part of the band gap. It is generally agreed that the less reactive metals such as Ag, Au and Cu yield barriers corresponding to pinning energies around 0.4 to 0.55 eV below E_c , though it is difficult to be certain which values are the true ones since they appear to depend on the measurement method and on whether the surface of the InP is clean or etched [21–26]. Some of the more reactive metals such as Al and Ni yield lower barriers on n-InP (higher on p-type) though precise barrier values again appear dependent on the method of measurement and nature of the surface. However, on clean surface many of the reported pinning energies are in the range 0.2–0.3 eV below E_c [14,17,20,26]. Other metals such as In and Sn also yield low barriers on n-InP under certain conditions. For the case of Sn we have previously reported low barriers (ohmic behaviour) when the metal is deposited at room temperature and higher barriers when deposited at 100 K. However, recent measurements [27] also yield barriers of 0.3–0.4 eV when deposited at room temperature. Metals like Pb also yield variable results on clean cleaved n-InP surfaces [28].

In the present work we have concentrated on contacts formed between Ga and InP(110) surfaces. The case of Ga is a particularly interesting one because previous studies [29] have suggested values of ≈ 0.6 eV for Schottky barriers (ϕ_b) on n-type crystals, and have also shown that the interface is a reactive one, i.e. it behaves chemically very much like the Al–InP interface. Ga–InP interfaces also show variations of ϕ_b with the nature of the InP surface which are important in tests designed to examine the various theories of interfaces discussed previously, and which are difficult to measure precisely for the lower barrier contacts.

In fig. 1 a series of I – V characteristics are shown for Ga contacts deposited on three different n-InP(110) surfaces, namely (a) etched surfaces (1% Br_2 in methanol), (b) air cleaved surfaces, and (c) atomically clean cleaved surfaces prepared by cleavage in ultrahigh vacuum. The set of curves shown was obtained on the same crystal and the differences observed, i.e. higher forward

and reverse currents for air cleaved surfaces, were reproducible in direction though not always in magnitude. At the higher forward voltages the current in all cases rises more slowly than for an ideal diode, as if the effective value of ϕ_b was voltage dependent. This makes an accurate evaluation of ϕ_b at zero voltage difficult. Nevertheless, if one extrapolates to zero voltage the reverse

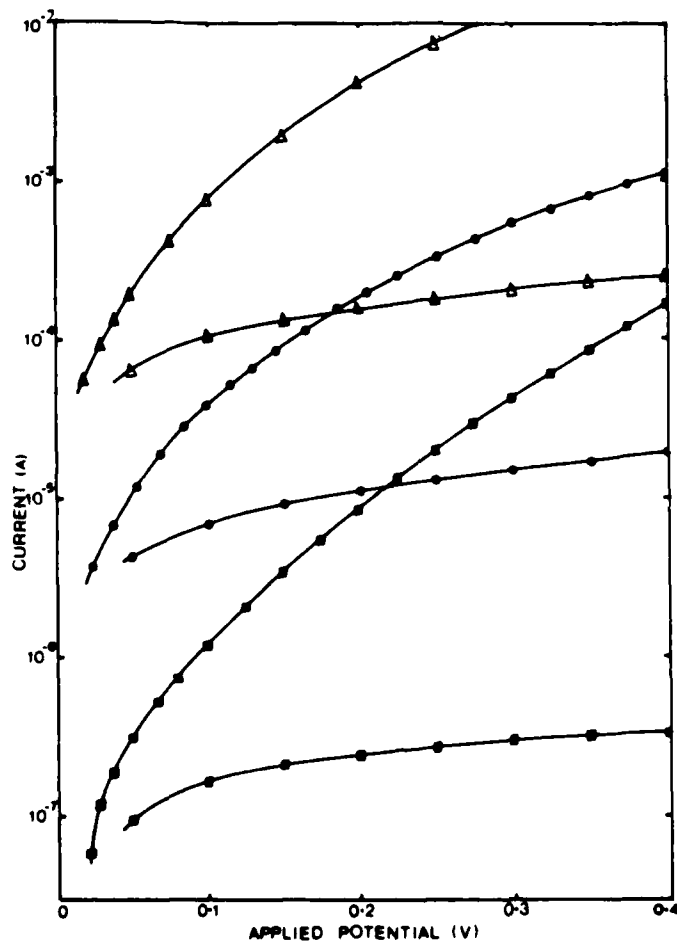


Fig. 1. Current-voltage (DC) characteristics for (a) Ga on chemically etched InP, \square ; (b) Ga on air cleaved InP, Δ , and (c) Ga on vacuum cleaved InP, \circ ; Schottky diodes.

currents, or the forward currents in the range 0.05–0.2 eV, values of ϕ_b of ≈ 0.65 , 0.58 and 0.50 eV are obtained for the etched, vacuum cleaved and air cleaved surfaces respectively, using a thermionic emission model. Although the accuracy of this procedure is limited it is clear from fig. 1 that the effective Schottky barriers are highly dependent on the nature of the surface being lowest for air cleaved surfaces and highest for etched ones.

The I - V curves shown in fig. 1 are typical of those for one crystal. More ideal I - V characteristics were obtained for another crystal and one of these is

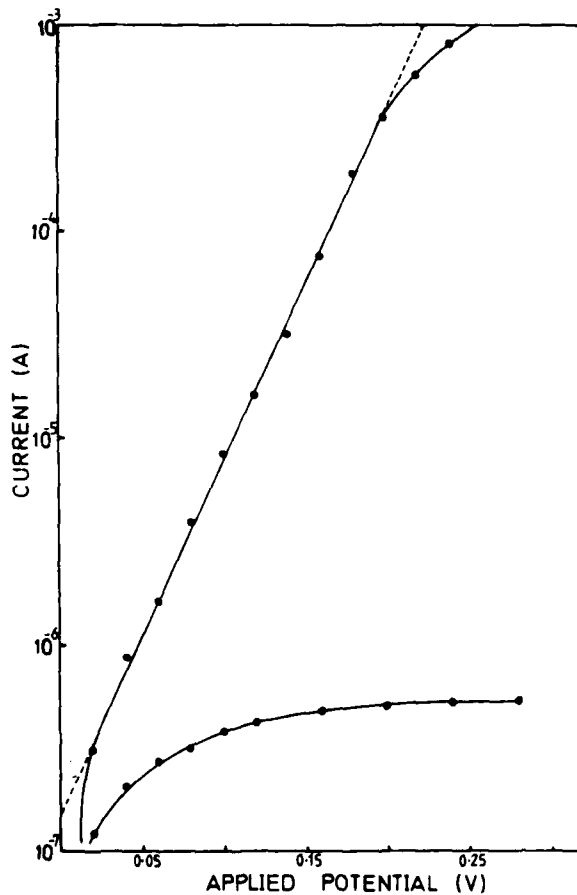


Fig. 2. Forward and reverse I - V characteristics of a high-quality Schottky diode obtained by evaporation of Ga on vacuum cleaved InP.

shown in fig. 2, for Ga deposited on a clean cleaved surface in a vacuum of $\approx 2 \times 10^{-10}$ Torr. A computer fit of this curve, using the thermionic emission theory, yields a non-ideality factor of 1.1 and a value of 0.6 ± 0.02 eV for ϕ_b . Most I - V curves on this crystal yielded barriers close to this value though in some cases the current at low voltages, presumably due to generation-recombination in the depletion layer, was a little higher than shown in fig. 2.

Attempts were also made to determine the Schottky barriers by the C - V technique for the diodes with I - V curves shown in fig. 1. However, the variation of capacitance with voltage was much smaller than for ideal diodes making determination of ϕ_b impossible. This behaviour is very similar to that often observed for Al on clean InP. Likewise the non ideal I - V behaviour is also commonly observed for Al on clean n-type InP(110), though in these cases the forward and reverse currents are almost equal and much larger in magnitude.

In conclusion it may be seen that metals on clean InP(110) surfaces yield a wide range of Fermi-level pinning energies, from ≈ 0.6 eV to ≈ 0.2 eV at least. The effective barriers formed are influenced by the precise nature of the InP surface being lower for air cleaved than for vacuum cleaved or etched faces for the case of Ga (and Al [31]) on n-InP crystals. It is of interest to note that although Ga behaves chemically very much like Al, the magnitude of the Ga-InP barrier is considerably larger than that for Al on InP although the reported work functions are similar for both Ga and Al [32]. As discussed later Ga also seems to yield higher values of ϕ_b in certain instances when deposited on clean GaAs surfaces [33].

3.2. Metals on cadmium telluride

In a previous publication [34] it has been shown that metals on clean cleaved n-type CdTe crystals yield a range of Schottky barriers as determined by I - V , C - V and UPS techniques. Indeed most metals previously studied [34] yielded ϕ_b values roughly in accordance with the Schottky model [4]. One metal, namely Ni, did not fit into this simple model. In the present studies we have extended these previous studies to include a range of other metals, namely Sb, Pd, Co, Cr and Fe and we have examined the dependence of the barriers formed on whether the surface is etched, air cleaved or atomically clean.

To illustrate a typical situation for overlayers on CdTe(110) surfaces consider the case of Sb, illustrated in fig. 3. These films were all deposited onto CdTe surfaces nominally at room temperature. The currents through the diode formed on an etched surface (using 1% Br₂ in methanol) is substantially lower than for the other two cases and the diodes formed are particularly stable. From the low-voltage section of the forward current characteristic we calculate a non-ideality factor of 1.11 and a value of 0.67 ± 0.05 eV for ϕ_b . A

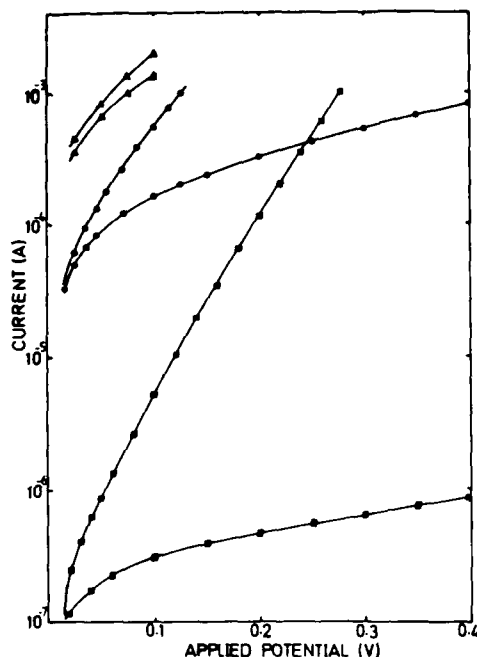


Fig. 3. Current-voltage (DC) characteristics for (a) Sb on chemically etched CdTe, \square ; (b) Sb on air cleaved CdTe, Δ ; and (c) Sb on vacuum cleaved CdTe, \odot .

similar value is also obtained by the C - V method as illustrated in fig. 4.

Sb overlayers on air cleaved CdTe yields barriers which are substantially smaller than on etched faces. In fact, as shown in fig. 3 the contact is practically ohmic, i.e. its effective barrier magnitude is less than ≈ 0.25 eV. Sb on an atomically clean surface leads to the I - V curve shown in the centre curves of fig. 3, which corresponds to a value of $\phi_b \approx 0.45$ eV. Fig. 4 shows the c^{-2} versus V profile which again yields a value of $\phi_b \approx 0.37$ eV.

Similar studies were conducted for Co, Cr, Pd and Fe and the results determined from the I - V characteristics are summarised in table 1. For vacuum cleaved surfaces Pd yields a value of $\phi_b \approx 0.4$ eV but the barriers for Co and Cr are lower with the I - V characteristic showing ohmic behaviour. We have also studied the formation of the Co-CdTe, Cr-CdTe and the Fe-CdTe interfaces in detail by ultraviolet photoelectron spectroscopy [35] and monitored the shift of the Fermi level at the surface for coverages below ≈ 30 Å, by observing the kinetic energies of electrons emitted from the Cd 4d core level. For the case of Cr and Fe no shift of the Fermi level was observed whereas for Co a small shift of ≈ 0.1 eV was seen consistent with a value of ϕ_b of ≈ 0.2 eV.

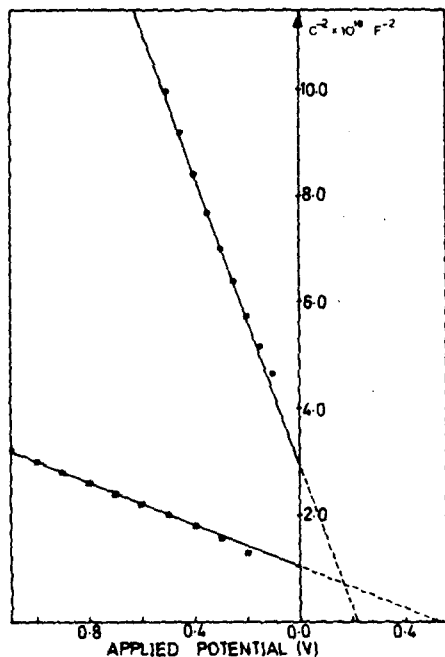


Fig. 4. Capacitance C^{-2} versus reverse voltage characteristics measured at 1 MHz for Sb on vacuum cleaved CdTe, \circ ; and Sb on chemically etched CdTe, \square ; Schottky diodes.

Table 1
Barrier heights, measured by I - V and C - V , of various metal-CdTe interfaces

Metal	Barrier height (eV)		
	Vacuum cleaved	Air cleaved	Chemically etched
Sb	0.4 ± 0.05	Ohmic	0.67 ± 0.05
Co	Ohmic	Ohmic	0.69 ± 0.05
Pd	0.4 ± 0.05	≈ 0.5	0.66 ± 0.05
Cr	Ohmic	≈ 0.3	Ohmic
Fe	Ohmic	Ohmic	0.63 ± 0.05

which would yield ohmic I - V behaviour. It should be noted that the Cd 4d emission splits as the metal overlayer thickness increases, consistent with dissociation of the surface, as discussed previously for the case of Ni [34].

Finally, we show in figs. 5a and 5b the Schottky barriers measured for the

range of metals on clean vacuum cleaved and on etched surfaces of CdTe respectively. These plots include data reported previously by our laboratory [34]. Barriers for etched surfaces are mostly in the range 0.6–0.7 eV in agreement with results reported by others [36]; however, the behaviour of Cr appears to deviate substantially from the remainder in that it gives ohmic contacts on etched surfaces (not included in fig. 5b). Metals on clean surface are seen to generate a wide range of barrier heights. With the exception of the transition metals the barriers formed are largely in accordance with the Schottky model, though it should be pointed out that gold is the only one yielding barriers larger than 0.5 eV for the range of non-transition metals used. Detailed considerations of these interfaces will be presented elsewhere but it should be noted here that most of them are disordered and are not atomically abrupt.

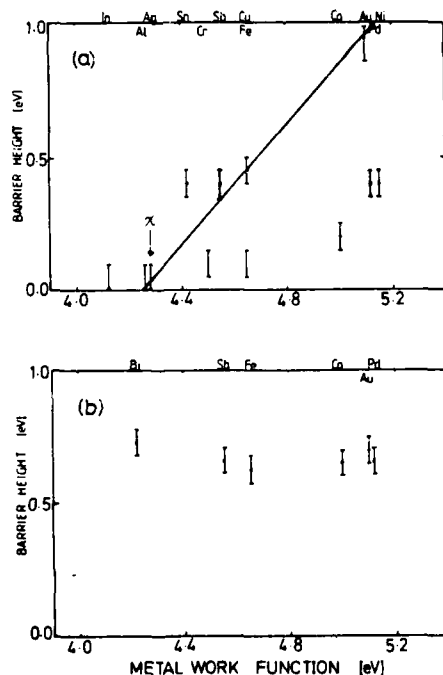


Fig. 5. Plot of barrier heights, ϕ_{b1} , versus metal work functions, ϕ_m , for various metals (a) on vacuum cleaved, (b) on chemically etched, CdTe interfaces. The electron affinity of CdTe (χ) is indicated on the plot. Some of the values were taken from ref. [34]. Note that Cr which is not included in fig. 5b gives contacts which are highly ohmic on etched surfaces.

4. Discussion

The results discussed in the preceding section illustrate quite clearly that metals on clean cleaved InP and CdTe surfaces yield a range of Schottky barriers so that the Fermi level is not pinned in just one position. Since the band gaps are reasonably close to that of GaAs it is of interest to compare the data obtained with those reported for metals on GaAs. As stated previously most metals evaporated onto a clean GaAs surface at room temperature correspond to an apparent pinning of the Fermi level in a narrow range of energy around 0.75–0.9 eV below E_c [5,37]. The ideality of the diodes formed are highly dependent on the nature of the GaAs surface [38]. The case of Ga on GaAs is a particularly interesting one since it has been reported to yield ohmic contacts to n-type crystals [39], ohmic contacts to p-type ones [40], and Schottky barriers of 0.75 eV [5] and 1.05 eV [33]. The work of Andersson et al. [33] in particular shows that effective barrier heights for Ga on n-GaAs are substantially larger than for similar Al contacts in accord with our observations for these metals on InP. Clearly, therefore, there are many similarities between the behaviour of metals on InP and on GaAs surfaces.

At the present time there is no complete agreement in the literature about the precise values of Fermi-level pinning energies for metals on InP, though it is generally agreed that they are nearly always in the upper half of the band gap. Early work by Williams et al. [30] suggested low effective barriers for metals which strongly reacted with the InP surface and reported higher barriers for these same reactive metals on chemically etched surface. Robinson et al. [17] more recently found low barriers for reactive metals for a chemically etched surface, and larger barriers for unreactive metals, consistent with previous trends on clean surfaces. Recently, Newman et al. [41] studied reactive and unreactive metals on clean and air cleaved surfaces and reported little difference between them. However, it is generally agreed that metals on InP do yield a range of Schottky barriers, and that the C - V and I - V characteristics are highly dependent on the precise nature of the interface. Reactive metals such as Al, Ni and Ga in particular tend to yield highly non-ideal diodes, and C - V profiles consistent with an interfacial layer where the effective Schottky barriers are dependent on bias. Soft X-ray photoemission has shown very clearly that disordered intermediate layers are formed at intimate interfaces as a result of chemical reactions. Recently also Evans et al. [42] have shown that similar reactions also occur for Al on air cleaved InP (and GaAs) in conjunction with a reduction of the oxide layer by the metal overlayer.

The present measurements on CdTe are in accord with earlier studies [34] and with similar studies on CdSe [43]. Again a wide range of barriers is observed for different metals and considerable dependence of the barriers on the nature of the surface is observed. It is of interest to note that the three

techniques of I - V , C - V and photoemission consistently yield similar values of the barrier (to within ≈ 0.1 eV) for a given metal on CdTe. This is somewhat different to the case of metals on InP where the intermediate layers formed often make barrier determination by C - V impossible.

We now consider the results for InP and CdTe in terms of two of the most promising models of Schottky barrier formation. Tersoff's model involving metal-induced gap states [9,10] indicates that the barriers will be determined by the semiconductor only, and predicts Fermi-level pinning above the valence band of 0.7 eV for GaAs and 0.76 eV for InP. For n-type solids at room temperature this yields Schottky barriers of 0.74 eV for GaAs and 0.58 eV for InP. These are in good agreement with experimental values for many metals on GaAs and for Ga on InP(110) surfaces and for some reported values with Au contacts also [21,44,23]. Pinning energies for metals on CdTe have not been reported by Tersoff. Oxide layers at the interface can, of course, separate the metal from the semiconductor sufficiently to prevent tunnelling of the metal wavefunctions into the semiconductor, in which case one may anticipate a greater dependence of barriers on the metal. This is contrary to our observations for etched CdTe. Of course the wide variation of Schottky barriers observed for metals on InP and CdTe clean surfaces appears also inconsistent with the Tersoff model.

The defect model assumes that pinning levels in the band gap at the surface of the semiconductor are generated when the metal overlayer is deposited, and these defect levels pin the Fermi level. The disorder, chemical reactions, and interdiffusion at many intimate interfaces suggest that defects may extend into the semiconductor some distance from the surface. Calculations suggest [12,13] that $\approx 10^{14}$ defects per cm^2 are needed for strong pinning and of course to pin effectively these must be a few Å from the semiconductor surface, since defect levels within the tunnelling range of the metal wavefunction (≈ 3 Å) will be screened. It has been argued that vacancies and antisite defects are generated by the chemical reactions and the disorder formed when Al overlayers are deposited on InP(110) and that these may be a source of pinning [5-7,45]. However, Ga overlayers appear to behave in a similar way to Al in soft X-ray photoemission experiments, yet the Ga-InP Schottky barriers are quite different from those observed at Al-InP interfaces, for both clean and etched surfaces. Clearly there exists a dependence of ϕ_b on the detailed nature of the metal even for metals which appear, at first sight, to behave similarly chemically. The large variations in ϕ_b for metals on CdTe could be interpreted according to the defect model provided several defect levels are involved. Alternatively it may be that the non-transition metals simply reflect the Schottky model with the transition metals being exceptions to this model. Clearly several defect levels are also required for the defect model to account for the results of metals on InP. It should be pointed out that the different barriers observed for Al and Ga on InP(110) surfaces are somewhat

inconsistent with the "anion cluster" model [46] since the common anion should lead to similar barriers in this model.

At the present time, therefore, the model of Tersoff does not appear consistent with our experimental data for InP and CdTe, and although the defect model is attractive several defect levels are necessary to account for the experimental data on the both semiconductors. In previous publications [2,6] we have suggested that many processes contribute simultaneously to Schottky barrier formation at intimate metal-semiconductor interfaces and indeed this view is consistent with the present studies. It is attractive to suggest that the primary Fermi-level pinning positions for metals on Si, GaAs and InP for abrupt perfect interfaces would be determined by the metal-induced gap states as suggested by Tersoff [9,10], but in reality defects cause deviations of the barriers from these "canonical" values. These defects include not only point defects such as vacancies and antisites but also more complex ones, and it must be remembered that the appropriate value of the work functions may not be those for the metals but those pertaining to the intermediate layer formed by chemical reactions, as suggested by Woodall and Freeouf [46]. To separate these various effects further detailed studies of these systems and others are necessary. At this stage we can only conclude that the metal-induced gap states model alone cannot completely account for the experimental data reported here for metals on InP and CdTe cleaved surfaces.

Acknowledgements

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Schottky-barrier height determination in the presence of interfacial disorder

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Abstract. By including the effects of electron-hole recombination and electron trapping in the analysis of the transport properties of Schottky diodes it is possible to obtain a more accurate estimate of the Schottky-barrier height. The magnitude of the barrier height obtained from an analysis of the forward I - V characteristics of CdTe Schottky diodes is in better agreement with that obtained from C - V measurements than that obtained by using the conventional procedure of introducing an ideality factor into the 'ideal diode' equation.

1. Introduction

Recently several quite different theories have been proposed to explain the magnitude of the Schottky barrier (ϕ_{SB}) present at the metal-semiconductor interface. However, at present, the uncertainties involved in the measurement of the Schottky-barrier height preclude a detailed comparison of the predictions of the models with the experimental data (Williams *et al* 1986). In this paper we demonstrate that the neglect of electron recombination and trapping in the analysis of the I - V curves of moderately doped Schottky diodes leads to a systematic error in the value of the barrier height obtained. By taking recombination and trapping into account explicitly a more accurate value of the barrier height can be obtained and the discrepancy between the value of the barrier height as calculated from I - V and C - V measurements is reduced.

The I - V characteristics of metal-semiconductor diodes are often termed 'ideal' if they can be described in terms of the thermionic emission of conduction electrons over the interfacial potential barrier alone. The I - V curve then has the form (Crowell and Sze 1966)

$$I = SA^{**}T^2 \exp(-\beta q \phi_{SB}) (\exp[\beta q(V - IR)] - 1) \quad (1)$$

where S is the contact area of the diode, A^{**} is the modified Richardson constant, ϕ_{SB} is the Schottky-barrier height, $\beta = 1/kT$ and R is the series resistance of the semiconductor. The saturation current I_s is given by $I_s = SA^{**}T^2 \exp(-\beta q \phi_{SB})$. However, a variety of physical processes can modify the form of the I - V curve. These include the recombination and trapping of electrons at states near the interface which have energies which lie in the semiconductor band gap (Shaw 1981), tunnelling through the potential barrier (Padovani and Stratton 1966, Crowell and Rideout 1969), the presence of interfacial layers (Crowell 1965) and the image force lowering of the potential barrier (Sze *et al* 1964).

The effect of the image force lowering can easily be

taken into account if the voltage dependence of the barrier height is linear. At a forward voltage V the barrier height $\phi_{SB}(V)$ will be $\phi_{SB} - \Delta\phi^0 + \alpha V$ where $\Delta\phi^0$ is the zero-voltage image force lowering and α is a dimensionless constant. By substituting $\phi_{SB}(V)$ into equation (1) and by restricting the forward voltage range to the region above $3kT/q$ and below the voltage at which the effect of series resistance becomes important equation (1) becomes

$$I \approx I_s' \exp(\beta q V/n) \quad (2)$$

where $n = (1 - \alpha)^{-1}$ and I_s' is given by

$$I_s' = SA^{**}T^2 \exp[-\beta q(\phi_{SB} - \Delta\phi^0)]. \quad (3)$$

The image force lowering of the potential barrier leads to values of n of approximately 1.04 for the Fe/n-CdTe diodes used in this study, and equations (2) and (3) can be used to calculate the Schottky-barrier height ϕ_{SB} of interfaces which are formed from moderately doped semiconductors which are free from surface oxide layers and defects which have energies which lie within the energy gap of the semiconductor. n is often called the 'ideality factor' and on a graph of $\ln I$ against V its introduction alters the gradient of the linear section of the curve. The factor n can therefore be defined as

$$n = \frac{q}{kT} \frac{\partial V}{\partial (\ln I)} \quad (4)$$

and it can be obtained from the gradient of a graph of $\ln I$ against V .

The above procedure for calculating the magnitude of the Schottky-barrier height is only valid for values of n of the order of 1.00-1.04. It is, however, frequently used to calculate ϕ_{SB} from graphs of $\ln I$ against V which have $n > 1.04$. Brillson (1981) has stated that 'extrapolating $\ln I$ to zero applied voltage in order to obtain ϕ_{SB} is not a reliable procedure for n values significantly different from one'. This is because the transport processes that cause deviation from 'ideal' behaviour have to be taken into

account explicitly if accurate estimates of ϕ_{SB} are to be made. To help clarify the problem I_s has been used to describe the saturation current that arises from the thermionic emission of electrons over the barrier and I_r to describe the value of the saturation current obtained from the application of equation (2). For small values of n ($n \leq 1.04$) they will be identical; however, when equation (2) is used to evaluate I_r from I - V curves that have $n > 1.04$ they will differ.

In many moderately doped Schottky diodes the most important contribution to the I - V characteristics, apart from that due to thermionic emission, is the contribution that arises from the recombination and trapping of electrons in localised states in the depletion region whose energies lie within the gap of the semiconductor. This has been considered in detail by Shockley and Read (1952), Hall (1952) and Sah *et al* (1957). The importance of recombination in Si diodes was first demonstrated by Yu and Snow (1968), who measured the temperature dependence of the forward current. Two activation energies were observed, the first at high temperature due to thermionic emission equal to $\phi_{SB} - V$ and the second at low temperature due to recombination equal to $\frac{1}{2}(E_g - V)$.

The efficiency of a recombination centre depends on its ability to capture both majority and minority carriers. The recombination rate is maximum when the centre lies at mid gap as this is the position that maximises the probability of *both* processes occurring. If the electron and hole capture cross sections can be considered equal it has been shown that the presence of a mid-gap recombination centre leads to a recombination current which is proportional to $(\exp(\beta q V / 2kT) - 1)$ (Grove 1967). The factor of two in the exponent arises directly from the assumption that the product pn under forward bias, throughout the depletion region, can be described by a function of form $pn = n_i^2 \exp(\beta q V)$ where p is the hole concentration, n is the electron concentration and n_i is the intrinsic carrier concentration. This is equivalent to assuming that the hole and electron non-equilibrium quasi-Fermi energies are flat and separated by qV throughout the depletion region. The recombination centres provide a parallel conduction path and the I - V characteristics contain an additional component. The total current can therefore be expressed approximately as

$$I = I_s(\exp[\beta q(V - IR)] - 1) + I_r(\exp[\frac{1}{2}\beta q(V - IR)] - 1) \quad (5)$$

where the magnitude of the recombination current I_r depends on the carrier lifetime within the depletion region (τ_r), the intrinsic carrier concentration and the depletion layer width (W):

$$I_r \approx Sq n_i W / 2\tau_r \quad (6)$$

For a semiconductor with a mid-gap recombination centre the carrier lifetime under forward bias has the value (Grove 1967)

$$\tau_r = (v_{th} \sigma n_i)^{-1}$$

where v_{th} is the thermal velocity, σ is the capture cross

section (which is assumed equal for holes and electrons) and n_i is the trap concentration. The ratio of the thermionic current to the recombination current is given by

$$\frac{2A^{**}T^2\tau_r}{qn_iW} \exp[\frac{1}{2}\beta q(V - 2\phi_{SB})]. \quad (7)$$

From equation (7) it can be seen that recombination is more important in diodes which have high barriers and low carrier lifetimes. Utilising the fact that the intrinsic carrier concentration is proportional to $\exp(-\frac{1}{2}\beta E_g)$ and neglecting the temperature dependence of the semiconductor energy gap it is relatively easy to see why Yu and Snow (1968) observed two activation energies by considering the temperature dependence of the two terms present in equation (5).

If the recombination term is included in the analysis of the I - V curves it is possible to account for values of n which are greater than one. The inclusion of the recombination term results in a reduction of the thermionic term necessary to fit the experimental curve. Values of n greater than one arise from the fact that the denominator of the exponent in the recombination term contains a factor of two. However, equation (5) is only a good description of the transport properties of moderately doped semiconductor-metal interfaces. For highly doped ($N_d \geq 10^{17} \text{ cm}^{-3}$) thermionic-field emission becomes important and it is necessary to include the effect of electrons tunnelling through the potential barrier at energies above the bottom of the conduction band. To determine the relative importance of thermionic emission to thermionic-field emission it is necessary to calculate the magnitude of the parameter E_{00} for the semiconductor in question (Padovani and Stratton 1966):

$$E_{00} = \frac{1}{2} q \hbar (N_d / \epsilon_s m^*)^{1/2} \quad (8)$$

where ϵ_s is the semiconductor dielectric constant and m^* is the electron effective mass. The size of E_{00} with respect to kT gives an indication of the relative importance of thermionic-field emission to thermionic emission. Except for very low values of forward voltage bias the thermionic-field emission contribution to the electron current has the form $I = I_s \exp(qV/E_0)$ where $E_0 = E_{00} \coth(\beta E_{00})$. For the diodes used in this study E_{00} was of the order of 2 meV. The onset of thermionic-field emission can be considered as an effective reduction in the barrier height $\Delta\phi$ (Rhoderick 1978) where $\Delta\phi = (3E_{00}/2q)^{2/3}(V_d)^{1/3}$ and V_d is the diffusion voltage. $\Delta\phi$ is approximately 0.02 V in these diodes. There are therefore good reasons for believing that under forward bias thermionic emission and recombination are the dominant transport processes in the moderately doped Fe/n-CdTe diodes used in this study.

If the recombination term is used it is necessary to use values of I_r which are comparable in magnitude with the value of I_s for diodes which have $n < 1.4$ to fit the curves measured experimentally. For $n > 1.4$, I_r can exceed I_s by many factors of ten. Then the assumption that the thermionic emission contribution is the dominant term is clearly unjustifiable and the use of the linear model to calculate the barrier height gives the wrong answer. In

most cases the error is reduced by the fact that the barrier height is logarithmically related to the saturation current:

$$\phi_{SB} = (\beta q)^{-1} \ln \left(\frac{SA^{**} T^2}{I_s} \right). \quad (9)$$

The use of the linear approximation to calculate the barrier height of Schottky barriers often results in a value for ϕ_{SB} which is smaller than that obtained by $C-V$ measurements, where the presence of traps does not influence the estimation of ϕ_{SB} if the differential capacitance is measured at a frequency that is well above the inverse response time of the traps. The application of the linear model presents another difficulty. Many of the $\ln I$ against V graphs have more than one region which can locally be described as linear. Furthermore, diodes which have a large series resistance may have no linear region whatsoever. Where then is it best to fit the linear model to the experimental points? In practice the choice is subjective and prone to a large degree of uncertainty. These difficulties have been discussed by de Sousa Pires *et al* (1985). The same authors have demonstrated that it is possible to fit the $I-V$ curves of Si Schottky diodes by using a computer model based on equation (5) which incorporates the effect of recombination. In this paper we consider the *magnitudes* of the Schottky-barrier heights obtained by such an analysis. Only thermionic emission and recombination have been taken into account. Other factors which contribute to the non-ideal behaviour such as electron tunnelling and the effect of interfacial layers have not been included. However, the basic model provides a satisfactory fit to a wide range of $I-V$ curves measured experimentally. We also provide guidelines for the optimal application of the linear model to obtain reliable estimates of the Schottky-barrier height.

2. Computer model

I_s , I_r and R have been determined for a set of experimental data points (V_i, I_i) by finding the best fit of equation (5) through the experimental data points. This was done by using an iterative procedure that minimises the sum of the squares of the residuals. To simplify the problem equation (5) was rearranged to make I the independent variable:

$$\hat{V}_i = I_i \hat{R} + \frac{2}{\beta q} \ln \left\{ \left[\frac{I_i}{I_s} + \left(1 + \frac{I_i}{2I_s} \right)^2 \right]^{1/2} - \frac{I_i}{2I_s} \right\} \quad (10)$$

where \hat{I}_s , \hat{I}_r , \hat{R} and \hat{V}_i are the estimates for I_s , I_r , R and V_i , respectively. The estimate for the voltage (\hat{V}_i) corresponding to current point I_i is compared with the experimental value (V_i). The estimators \hat{I}_s , \hat{I}_r and \hat{R} are determined by using a sequential iterative procedure to minimise f , the sum of the squares of the voltage residuals:

$$f = \sum_{i=1}^N (V_i - \hat{V}_i)^2 \quad (11)$$

where N is the total number of data pairs. At the start of the iteration I_s was chosen by using a linear least-squares fit to the experimental data. I_r was defaulted equal to I_s ,

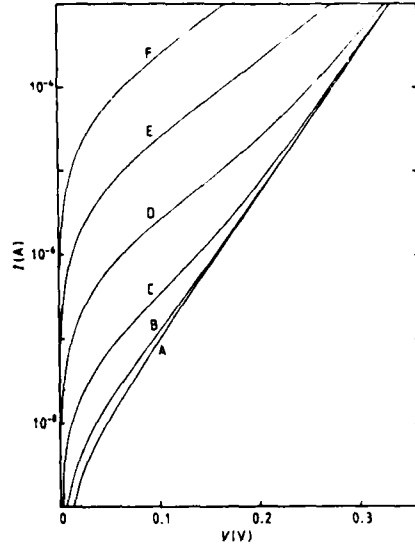


Figure 1. Curve A represents the forward $I-V$ curve of an 'ideal' diode with $n = 1$ and $I_s = 2 \times 10^{-9}$ A. The other curves, B, C, D, E and F, have had recombination terms added with I_r values of 4×10^{-9} , 4×10^{-8} , 4×10^{-7} , 4×10^{-6} and 4×10^{-5} A, respectively.

and R was easily estimated from the high forward bias part of the $I-V$ curve.

A qualitative understanding of how the thermionic and recombination terms combine can be obtained from figure 1. Curve A represents an ideal diode with $n = 1$ and $I_s = 2 \times 10^{-9}$ A. Curve B was obtained by adding a recombination term which had $I_r = 4 \times 10^{-9}$ A. Curves C, D, E and F were obtained by adding recombination terms with $I_r = 4 \times 10^{-8}$, 4×10^{-7} , 4×10^{-6} and 4×10^{-5} A, respectively. The addition of the recombination term causes a reduction in the gradient of the $I-V$ curve on a logarithmic plot and an increase in the factor n at low forward bias. This is shown in figure 2, where n has been calculated for a number of points in the voltage range 0–0.4 V. The reciprocal of n is simply a measure of the gradient of the $\ln I$ against V graph. The application of the linear model results in an overestimate of the saturation current ($I_s' > I_s$) and an underestimate of the Schottky-barrier height. The linear model has been applied to the curves B, C, D, E and F using a linear least-squares fit to 21 equally spaced points in the voltage range 0.1–0.3 V. The resulting values of I_s' and n are summarised in table 1. It is apparent from the shape of the curves in figure 1 that the upper region of the $I-V$ curve will give the best estimate of ϕ_{SB} if the linear model is used. This approach has in fact been used by Thanailakis (1975) to estimate ϕ_{SB} from low-temperature $I-V$ characteristics. However, this region is often obscured by the effect of series resistance for diodes with low barriers and the process of extrapolating to obtain the saturation current I_s' is not as accurate as a computer fit to equation (5). By calculating

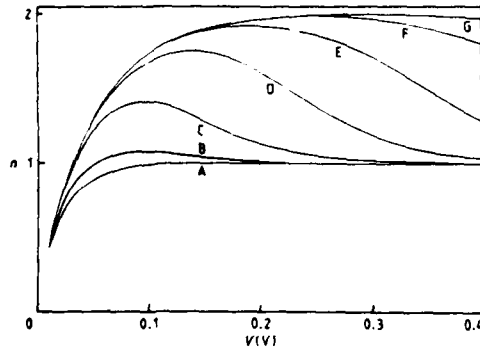


Figure 2. The local n factor has been calculated for curves A–F of figure 1. Also shown (curve G) is the local n factor for a recombination component of $I_s = 4 \times 10^{-6}$ A.

Table 1.

Curve	n^\dagger	$I_s'(\text{A})$	$I_s(\text{A})$	$I_r(\text{A})$
B	1.03	2.5×10^{-8}	2.0×10^{-9}	4.0×10^{-8}
C	1.18	9.9×10^{-8}	2.0×10^{-9}	4.0×10^{-8}
D	1.60	2.0×10^{-7}	2.0×10^{-9}	4.0×10^{-8}
E	1.88	3.1×10^{-6}	2.0×10^{-9}	4.0×10^{-8}
F	1.94	3.4×10^{-5}	2.0×10^{-9}	4.0×10^{-8}

$^\dagger n$ has been calculated by finding the best linear least-squares fit of equation (2) to curves B–F of figure 1 using 21 equally spaced points in the voltage range 0.1–0.3 V.

the ideality factor, as before, for an ideal diode which has varying degrees of recombination added it is possible to determine the relationship between the predicted saturation current (I_s') and n . This is summarised in figure 3, where the value of n , calculated by using a linear least-squares fit to 21 equally spaced points in the voltage range 0.1–0.3 V (curve B) and to 11 points in the range 0.2–0.3 V (curve A), has been plotted against the ratio of I_s' to I_s . An empirical relationship exists between n and

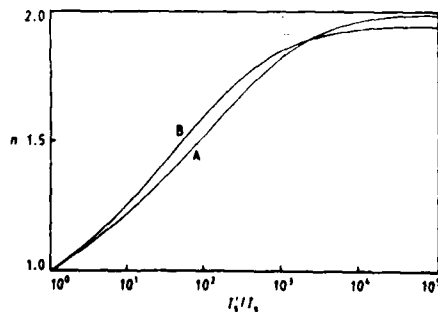


Figure 3. The relationship between n and the ratio I_s'/I_s as calculated by using a linear least-squares fit to 11 equally spaced points in the voltage range 0.2–0.3 V (curve A) and to 21 points in the range 0.1–0.3 V (curve B).

I_s'/I_s and the ratio I_s'/I_s can be determined once n is known. Therefore I_s can be determined once n and I_s' have been extracted from the experimental data. The linear model has been fitted over two separate ranges to illustrate that the relationship between n and I_s'/I_s is not unique and does depend on where the fit is made. If a linear least squares fit is made in the voltage range 0.1–0.3 V then the following approximate relationship can be used to estimate the value of the saturation current:

$$I_s \approx I_s' 10^{(c-n)/m} \quad (12)$$

where $c = 1$ and $m = 0.26$ for $n < 1.20$ and $c = 0.91$ and $m = 0.34$ for $1.20 < n < 1.75$. Substituting this into equation (9) results in the following expression for the Schottky-barrier height:

$$\phi_{SB} \approx \phi_{SB}' + 2.303 \frac{(n-c)}{m} \frac{1}{\beta q} \quad (13)$$

where ϕ_{SB}' is the barrier height as calculated using equation (9) with $I_s = I_s'$ and the second term is the recombination correction. Equation (13) is presented primarily to demonstrate that the recombination correction to the Schottky-barrier height is linearly proportional to the calculated value of n . However, equation (13) can be used to estimate the magnitude of the recombination correction to ϕ_{SB} for diodes fabricated on moderately doped semiconductors. This will be considered in more detail in the next section.

3. Experimental results

We have investigated experimentally the I – V and C – V characteristics of moderately doped Fe/CdTe Schottky diodes which exhibit non-ideal behaviour at room temperature with ideality factors in the range 1.04 to 1.98. The Schottky-barrier heights $(\phi_{SB})_{IV}$ for the Fe/CdTe diodes as measured using the linear approximation (equation (2)) vary from diode to diode and are always lower than the barrier heights obtained from C – V analysis, $(\phi_{SB})_{CV}$.

The CdTe used in this sequence of experiments was In doped with a carrier concentration of approximately 10^{16} cm^{-3} . The CdTe was mechanically polished, chemically etched in 1% bromine-methanol and then thoroughly rinsed in methanol. The samples were transferred to a high vacuum system and Fe was thermally evaporated at a pressure of better than 10^{-6} Torr. Ohmic contacts were made using an In/Ga alloy. Although our analysis of the forward I – V curves has not included the effect of an insulating interfacial layer, the value of the barrier height obtained from several Fe/CdTe diodes using conventional C – V analysis is very reproducible and is in good agreement with $(\phi_{SB})_{IV}$. This suggests that the layer does not attenuate thermionic emission significantly.

The dark forward I – V characteristics of three Fe/CdTe Schottky diodes (D1, D2 and D3), measured at room temperature, are shown in figure 4. The ideality factor and the barrier height $(\phi_{SB})_{IV}$ calculated using the linear model together with the barrier height $(\phi_{SB})_{IV}$

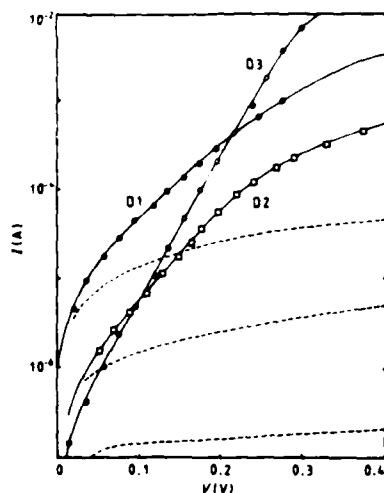


Figure 4. The points represent the I - V curves of three Fe/CdTe Schottky diodes (D1, D2 and D3) measured experimentally and the full curves are the calculated best fits of equation (5) through the data points. In each case the contact areas were circular with a diameter of 1 mm. The broken curves indicate the position of the reverse biased current for each diode.

Table 2.

Sample	Linear model		Computer fit ($\phi_{ss} _V$ (V))	C-V ($\phi_{ss} _V$ (V))
	n	($\phi_{ss} _V$ (V))		
D1	1.98	0.56	0.73	0.73
D2	1.60	0.63	0.72	—
D3	1.05	0.67	0.69	0.72

obtained by finding the best fit of equation (5) through the experimental points are listed in table 2. Figure 5 shows the plot of (capacitance) $^{-2}$ as a function of bias voltage for two of the above diodes (D1 and D3) measured at 1 MHz. The barrier heights ($\phi_{ss}|_V$) $_{CV}$ obtained from these plots by using a linear least-squares fit to the data points are also listed in table 2. No correction has been made in either case for the image force reduction in the barrier height which is approximately 0.02 V for these diodes. The three diodes represent the range of I - V and C- V curves obtained from Fe/CdTe Schottky diodes, with D1 and D3 representing the two extremes.

The results presented in table 2 can be used to test equation (13). For example, by fitting equation (5) to the I - V curves of diodes D2 and D3 it was found that the recombination corrections to the Schottky-barrier height ($\Delta\phi_{rec}$) were 0.09 V and 0.02 V, respectively. At room temperature equation (13) can be written as $\Delta\phi_{rec} = 0.226(n-1)$ for $n < 1.2$ and as $\Delta\phi_{rec} = 0.173(n-0.91)$ for

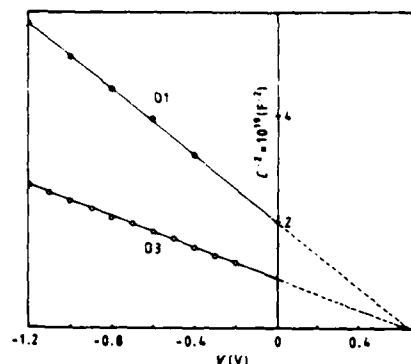


Figure 5. C^{-2} as a function of applied voltage for diodes D1 and D3 of figure 4. The gradient of the lines has been calculated by using a linear least-squares fit to the experimental points.

$1.2 < n < 1.75$. The values of $\Delta\phi_{rec}$ expected for D2 and D3 are therefore 0.12 V and 0.01 V, respectively, which are in reasonable agreement with the results of the computer fit. It should be emphasised at this stage that equation (13) has been derived by assuming that the barrier height is independent of voltage. This is not always a good assumption. For example, if there is a continuous insulating oxide layer at the interface n will depart from unity. However, the reasonable agreement between the results of the computer fit and the results of equation (13), together with the fact that equation (5) can be fit very well to the I - V characteristics over a wide voltage range, suggest that the oxide layer is *discontinuous* and that it does not cause n to depart appreciably from unity. Therefore, if equation (13) is used to estimate $\Delta\phi_{rec}$ for a diode which has a voltage-dependent barrier height, it will result in an overestimate of $\Delta\phi_{rec}$. This is because the voltage dependence of ϕ_{ss} will result in an increase in n for all forward voltages.

The observed variation in the I - V curves contains two components. Firstly, for a single CdTe crystal there is a variation due to the local quality of the semiconductor surface. Secondly, there is a variation from crystal to crystal which depends upon the bulk crystal quality. Both the local nature of the semiconductor surface and the bulk quality of the semiconductor crystal are important in determining the magnitude of the carrier lifetime τ , within the depletion region. This is illustrated quite well in figure 4. Diodes 1 and 2 were fabricated on the same CdTe crystal, which was of inferior quality to the CdTe crystal used to fabricate diode 3. In each case the crystal of inferior quality produced I - V curves with a large recombination component and a high value of n . The application of the conventional approach of estimating ϕ_{ss} , based on equation (2), to the I - V curves of diodes which have been fabricated on crystals of different quality often results in a range of Schottky-barrier heights (see table 2, for example).

4. Discussion

By including the effects of recombination and trapping in the analysis of the forward I - V characteristics of moderately doped Schottky barriers it is possible to obtain a more accurate estimate of the Schottky-barrier height. As a result the magnitude of the Schottky-barrier height is increased and is in better agreement with the value of the barrier height obtained from C - V analysis. However, although the inclusion of the recombination term reduces the discrepancy that is often present between $(\phi_{SB})_{IV}$ and $(\phi_{SB})_{CV}$ (see, e.g., Waldrop 1984, Thanailakis 1975, Thanailakis and Rasul 1976, Amith and Mark 1978), in many cases $(\phi_{SB})_{IV}$ is still smaller than $(\phi_{SB})_{CV}$ and the reasons for this will be discussed briefly later.

In this study the effect of the image force lowering of the potential barrier on the I - V curves has been totally neglected. This is because the image force correction to the thermionic term has a relatively small effect on the total I - V curve when compared with the recombination contribution in the presence of a large degree of disorder. If equation (5) is used to describe the I - V curves of nearly ideal diodes then the effect of the image force must be included in the thermionic term. However, in such cases it is unnecessary to use a curve-fitting procedure to estimate ϕ_{SB} as the conventional approach of using a linear fit to the $\ln I$ against V graph provides an accurate estimate of the Schottky-barrier height.

In conclusion, by incorporating the effects of recombination unambiguous estimates of the Schottky-barrier height can be obtained from the I - V curves of moderately doped Schottky diodes. The photoresponse technique also gives unambiguous results for interfaces which are free from insulating layers providing the corrections that have been discussed by de Sousa Pires (1978) are incorporated in the analysis. Conventional C - V analysis essentially uses a measurement of the interfacial differential capacitance under reverse bias to obtain an estimate of the forward voltage which flattens the semiconductor bands. It should be emphasised that the C - V technique does not measure the diffusion voltage directly but infers it from a measurement of the reverse bias behaviour of the interface. If the potential barrier does not rise parabolically towards the metal but is for some reason lowered at the interface the C - V technique will result in an overestimate of the barrier and provide an estimate of the intrinsic barrier height, the barrier height in the absence of the lowering mechanism. In addition, conventional C - V analysis does not take into account the effects of charged interfacial defect distributions or non-planar, stepped or faceted interfaces, all of which may influence the determination of ϕ_{SB} . Furthermore, a plot of C^{-2} as a function of V does not always give a clear indication that any of these effects are important. It is assumed that the depletion width is a well defined quantity and that the donor distribution is uniform. However, there is often a high degree of intermixing at the metal-semiconductor interface which renders the

depletion approximation a less accurate description of the microscopic structure. Carefully analysed I - V characteristics provide good agreement with the results of the photoresponse technique and provide a measure of the Schottky-barrier height. The C - V technique provides a measure of the intrinsic barrier height which will be close to the actual barrier height if the barrier has a parabolic profile right up to the interface.

The agreement obtained between $(\phi_{SB})_{IV}$ and $(\phi_{SB})_{CV}$ for a range of Fe/n-CdTe diodes is better than was expected as our analysis has not included the effect of insulating layers. However, the diodes used in this study exhibited linear C^{-2} - V characteristics and it has been suggested that the oxide layer is in fact discontinuous and incapable of supporting an appreciable potential difference. This conclusion has been borne out by a study of Schottky-barrier formation on oxidised CdTe surfaces using soft x-ray photoemission with synchrotron radiation and is discussed elsewhere (Dharmadasa and Williams 1986).

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Metals on cadmium telluride: Schottky barriers and interface reactions

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The Schottky barriers formed for a wide range of metals on (110) *n*-CdTe surfaces have been studied using current-voltage and capacitance-voltage techniques. The surfaces were prepared by cleaving in ultrahigh vacuum, cleaving in air, and chemical etching. The electrical barriers are drastically influenced by oxide layers on the surface. Most metals on the chemically etched surfaces yield barriers having values around 0.7 eV but Mn, Cr, and V are notable exceptions, yielding ohmic or low barrier contacts. Microscopic interactions of these interfaces have also been studied by soft x-ray photoemission using synchrotron radiation. Detailed comparisons of the microscopic interaction of Ag and Mn with the clean and oxidized surfaces, using photoemission, are presented. In contrast to the behavior of Ag, the Mn overlayer completely reduces the CdTe native oxide layer, resulting in lower barrier contacts.

A full understanding of the formation of electrical barriers at metal-semiconductor interfaces still eludes us after several decades of research. During the last few years, though, considerable progress has been made mainly as a result of the application of modern surface science techniques to probe microscopic interactions at metal-semiconductor interfaces. These studies have shown that complex microscopic interactions are common at intimate interfaces and there have been attempts to relate these interactions to the formation and the magnitude of the Schottky barrier heights at metal-semiconductor junctions.¹⁻³ So far these studies have been only partly successful.

The conventional Schottky model indicates that the barrier height at metal-semiconductor interfaces should be highly dependent on the work function of the metal contact and therefore large variations of barriers should be expected for different metals on a given semiconductor.⁴ However, this is not so in practice: for a large range of metals on the most common semiconductors, namely, Si, GaAs, and InP, the Schottky barrier heights vary by no more than around 0.4 eV.⁵ For the case of metals on GaAs it appears that the presence of thin oxide layers at the metal-semiconductor interface does not have a significant influence on the magnitude of the barrier height formed at least for a number of metals (which includes Au, Ag, Cu, and Al).⁶ However, for the case of metals on InP it has been reported that thin oxide layers at the interface may have a very dramatic effect on the electrical nature of the interface and on the Schottky barriers formed.⁷ These observations have been used as evidence for and against some of the more popular models of Schottky barrier formation which are currently available. For example, it has been suggested that the observation that thin oxide layers at metal-GaAs interfaces appear to have little effect on the barrier height means that a defect model⁸ is to be favored over the model involving metal induced gap states.⁹ However, these arguments are rather dependent on whether or not the metal overlayers chemically interact with the oxide layer and little information is available at the present time relating to these detailed interactions.

In this letter we investigate the Schottky barriers formed by a wide range of metals deposited on cleaved (110) CdTe

surfaces. It has been previously shown that this system yields a wide range of barrier heights for different metals and is a rather useful one in order to probe the validity of some of the models of Schottky barrier formation currently available.⁷ In this letter we have extended previous studies to a much wider range of metals and we have studied the interfaces formed in considerable detail. We have also investigated the influence of intermediate oxide layers at the metal-CdTe interfaces and we show that these oxides have a dramatic effect on the barrier heights formed for almost all metals studied. However, there are some notable exceptions, namely, Mn, Cr, and V and we discuss this in terms of the microscopic interactions between the metal overlayer, the semiconductor, and the oxide layers.

The *n*-type single crystals of CdTe used in the experiments were grown by both fast vertical Bridgman methods and the solvent evaporation technique. The crystals were doped with indium and the carrier concentration was in the range of 10^{16} to 10^{17} cm⁻³. Three types of surfaces were studied: (a) vacuum cleaved, (b) air cleaved, and (c) chemically etched. Crystals with appropriate ohmic back contacts were mounted in an ultrahigh vacuum system and clean (110) surfaces were obtained by cleaving the crystals at a pressure of approximately 10^{-10} Torr. Appropriate contacts were then deposited on to these clean surfaces by evaporating the appropriate metal from a carefully outgassed filament. Oxidized surfaces were prepared either by cleaving the crystal in air or by chemical etching in (a) 1% bromine in methanol solution and (b) 1% bromine in methanol followed by 1N KOH in methanol. The latter treatment has been found necessary to remove excess tellurium from the etched surface.^{10,11} Metal contacts were deposited onto these oxidized surfaces at a pressure of approximately 10^{-8} Torr. Schottky barriers were investigated by current-voltage (*I-V*) and capacitance-voltage (*C-V*) techniques at room temperature with external light excluded. For metals on the atomically clean surfaces the formation of the Schottky barrier has also been probed by ultraviolet photoelectron spectroscopy for metal coverages below about 20 Å. Full details of these experiments will be presented elsewhere.¹²

The microscopic interactions at the metal-CdTe inter-

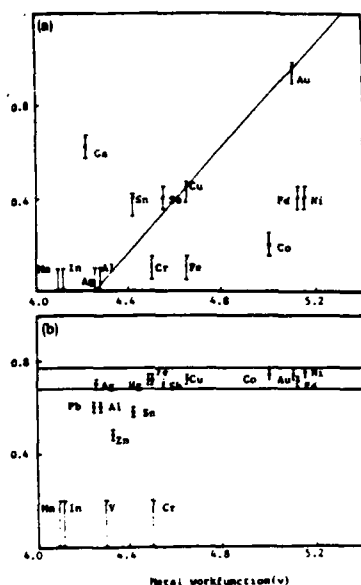


FIG. 1 Plot of Schottky barrier heights, ϕ_B , vs metal work functions, ϕ_m , for (a) metal-vacuum cleaved CdTe and (b) metal-chemically etched CdTe interfaces.

faces were studied by soft x-ray photoemission using the synchrotron radiation source at Daresbury laboratory. The experiments were performed using a standard ultrahigh vacuum apparatus equipped with a double pass cylindrical mirror analyzer. Controlled amounts of metal ranging from a small fraction of a monolayer upwards were evaporated onto the surface of CdTe in a controlled manner at a pressure of about 2×10^{-10} Torr. The monochromator used was a grazing incidence instrument described elsewhere and the energy resolution was about 0.3 eV at a photon energy of 100 eV.

Figure 1(a) shows the Schottky barrier heights measured for a range of metals on clean cleaved CdTe surfaces; the barrier heights have been plotted against the metal work function. This plot includes data previously reported¹¹ by our laboratory as well as new data for a wide range of metals. Barriers smaller than about 0.3 eV were too low to be measured by I - V and C - V methods and the values shown in Fig. 1(a) are based on core level shifts in UPS experiments. In previous reports it was suggested that the data for In, Al, Ag, Sn, Cu, and Au are in reasonable accordance with the conventional Schottky model but Ni was a clear exception. It may be seen from Fig. 1(a) that indeed there are many more exceptions also, i.e., Cr, Fe, Co, Pd, and Ga. In addition, in the present studies we find that Au often yields barriers of around 0.6 eV rather than the 0.9 eV shown. This additional data suggests that a multilevel pinning mechanism may be just as appropriate as the Schottky description for metals on clean cleaved CdTe. The wide variation observed for Au is believed to be associated with the formation of a Cd-Au alloy.¹⁴

The Schottky barrier heights obtained for a range of metals on chemically etched CdTe surfaces are shown in Fig. 1(b), again the horizontal scale represents the metal work function. Most of the metals, namely, Ag, Hg, Fe, Sb, Cu, Co, Au, Ni, and Pd yield a fairly constant barrier height of around 0.7 eV as determined by current-voltage measurements. These diodes show good rectification properties and their ideality factors vary from 1.05 to 1.98. Diodes prepared with Ag, Hg, Cu, and Au always produce somewhat higher barriers when measured by the C - V technique; detailed considerations of this point will be presented in a later paper.¹⁵ For the other metals concerned C - V and I - V data gave values of barrier height in close agreement provided the effect of recombination and generation at the interface was properly taken into account.¹⁶ Mn, V, and Cr always produce very low barriers as indeed they do on the clean surfaces. Another group of metals, namely, Pb, Al, Zn, and Sn, produces barriers which are somewhat less than 0.6 eV but are highly irreproducible. The values shown in Fig. 1(b) are typical examples but these are subject to large variations depending on how precisely the contact is prepared. The surfaces that have been treated with 1N KOH in methanol produced barriers of very similar heights to those prepared with only the 1% bromine in methanol etch, but in general surfaces treated with the former etch tend to give diodes with better reverse saturation current characteristics and improved rectification factors. When metals are deposited on air cleaved CdTe surfaces the barriers measured are extremely variable and again depend on precisely how the contact is fabricated. The noble metals Au, Ag, and Cu produce higher barriers than those obtained for the same metals on clean surfaces and again the transition metals Co, Fe, V, Cr, and Mn produce extremely low barriers and contacts which appear ohmic. In general the barriers appear to be dependent on the thickness of the oxide layer.

Clearly, therefore, metals on CdTe surfaces yield a wide range of Schottky barrier heights and these in turn are significantly influenced by the presence of intermediate oxide layers. The range of barriers measured is larger than those reported for similar metals on III-V semiconductors. It is quite obvious that the Schottky model⁴ alone does not account for the data in Fig. 1, and it is also obvious that the metal induced gap states (MIGS)¹⁷ model, in its elementary form at least, cannot account for the large variations of ϕ_B , and the way they are influenced by oxide layers. Since it is known that most of the intimate interfaces are disordered and non-abrupt a Fermi level pinning model involving defect levels appears to be more appropriate.⁸ At this stage, however, it would be premature to speculate about the detailed nature of such defect levels.

Of particular interest in Fig. 1 is the fact that Schottky barriers formed for some metals on CdTe are drastically influenced by oxide layers whereas others are not. This contrasts to the case of similar metals on clean and oxidized GaAs and merits further consideration. We have therefore studied the microscopic interactions at these interfaces for a range of metals and report here on two representative examples. These are Ag, which is significantly influenced by oxide layers, and Mn which is not.

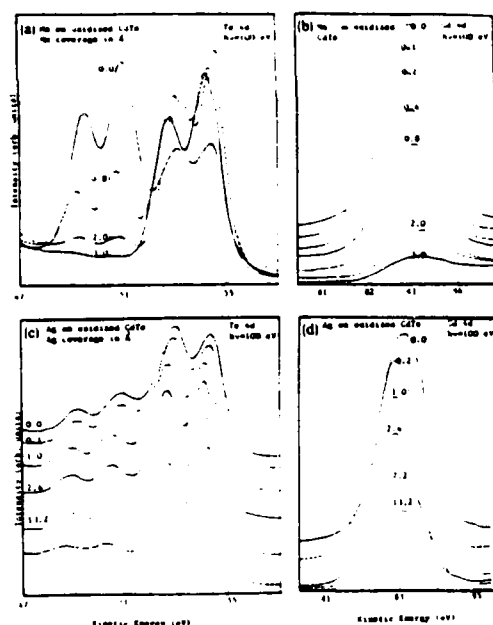


FIG. 2. Flux-normalized photoemission spectra of the Te 4d and Cd 4d core levels with increasing coverages of Mn and Ag, taken at photon energy of 100 eV.

Figure 2 shows soft x-ray photoemission data for oxidized CdTe and following the deposition of small amounts of Mn and Ag. The core level emission associated with the Cd 4d and Te 4d are shown. On the oxidized surface the Te 4d $\frac{3}{2}$ and 4d $\frac{5}{2}$ emission shows large chemically shifted (~ 3.6 eV) components associated with Te in a TeO₂ environment. Consider the deposition of Ag onto this oxidized surface as shown in the lower panels. In this case the TeO₂ layer is thin (~ 1.5 Å) and it is still present even after the deposition of 13 Å of Ag on the surface. The behavior for Mn, though, is entirely different, as shown in the upper panels. Here the oxide is entirely reduced from TeO₂ for very small coverages of Mn. In the upper panel of Fig. 2 we have chosen an example where the oxide layer is thick (~ 3.0 Å) and the dramatic effect, where the intensity of the Te elemental emission increases at the expense of the oxide, is clearly visible. It may be noted that the Cd 4d emission suffers a progressive decrease in intensity with increasing thicknesses of the Mn overlayer. Clearly, Mn reduces the oxide layer rapidly, presumably to form Mn₂O₃, which may allow the metal to make intimate contact with the CdTe

surface yielding values of ϕ_b similar to those for Mn on clean CdTe surfaces. For silver, on the other hand, the oxide layer separates the metal from the intimate CdTe surface, and the barrier is determined by the oxide-CdTe interface. A good estimate of the chemical reactivity of various metals with the native oxides of CdTe can be obtained on the basis of published bulk thermodynamic data.¹⁵ It is of interest to note that values of ϕ_b of ~ 0.6 eV are obtained also with oxidized n-CdTe-electrolyte interfaces.¹⁷ These studies, therefore, strongly indicate that the different effect of the oxide layer for different metals on CdTe is associated with dissimilar interactions of those metals with the oxide layer.

In conclusion, we have shown that metals on n-CdTe crystals yield a wide range of Schottky barriers which is inconsistent with the Schottky model as well as the MIGS model. The data are more consistent with models involving imperfections such as defects and mixed phases at the interfaces. The barrier heights are significantly influenced by oxide layers, although some metals are clear exceptions. Studies of the microscopic interactions for two metals, namely, Mn and Ag, indicate that these differences are associated with a strong reduction of the oxide by some metals but not by others.

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MICROSCOPIC AND MACROSCOPIC STUDIES OF METAL-SEMICONDUCTOR
SCHOTTKY BARRIERS AT METAL-CdTe JUNCTIONS

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INTRODUCTION

The formation of stable and reliable contacts to semiconductors is of the utmost importance in microelectronics technology, yet the physics of such contacts is not well understood. Recent theories of Schottky barrier formation involve mixed phases and defects at the metal-semiconductor interface, and also the generation of metal induced gap states (MIGS) in the semiconductor. In these models, as well as in the conventional Bardeen model, interface state densities of $\sim 10^{14} \text{cm}^{-2}$ yield strong pinning of the Fermi levels and, for metals on compound semiconductors in particular, these different mechanisms may compete with the relative importance of each depending on the details of the contact fabrication. In this paper we describe measurements of Schottky barrier heights and microscopic interactions at metal-CdTe interfaces. CdTe has a similar band gap to GaAs and on the basis of Fermi level pinning by MIGS one might anticipate similar Schottky barrier behaviour for the two materials. A wide range of metals on n-GaAs yield values of ϕ_b between 0.6 eV and 0.9 eV and it has been reported that these values are not significantly influenced by oxide layers at the interface, i.e. similar ϕ_b 's are obtained whether the metal is deposited on clean or oxidised surfaces.⁽¹⁾ In this paper we show that the situation for CdTe is very different and is not consistent with MIGS theories in their most elementary forms.

RESULTS

Figure 1 shows measured Schottky barrier heights for metals on clean, air cleaved and chemically etched (using Br in methanol) n-CdTe crystals. Data for some of these metals have been published previously.^(2,3) Several points may be made:- (a) The low barrier heights are subject to large inaccuracies since they were too low to be measured by I-V and C-V methods and, where possible, were determined by photoelectron spectroscopy. However, this is often difficult due to 'chemical shifts' associated with the core level photoemission. (b) All values of ϕ_b greater than 0.4 eV in Figure 1 were obtained by the I-V method. Great care was taken to correct for generation-recombination currents⁽⁴⁾ and values of ϕ_b determined by C-V were in reasonable agreement to those derived from I-V method, in most cases.⁽⁵⁾ (c) Au consistently appears to yield values of ϕ_b close to 0.9 eV

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or close to 0.6 eV on clean surfaces. This two valued result is also consistently found for Au and Sb on chemically etched CdTe.

(d) Metals such as Cr, V and Mn yield low values of ϕ_b for clean and oxidised surfaces. Au forms large barriers in both cases. These metals appear little influenced by the existence of an oxide layer a few Å thick. (e) For another group of metals the measured Schottky

barrier height is significantly influenced by the nature of the surface. One group (Ag, Hg, Fe, Sb, Co, Cu, Ni and Pd) appear to give reproducible values of ϕ_b of around 0.7 eV on chemically etched surfaces. They are less reproducible on air cleaved surfaces, as indeed are the values for another group (Cd, Pb, Ga, Al, Sn) on chemically etched surfaces.

In order to examine these effects further, the detailed microscopic nature of the metal-CdTe interfaces have been investigated by photoelectron spectroscopy, using the synchrotron radiation source at Daresbury. Detailed studies of the interactions of a range of metals will be presented elsewhere.^(3,5) Here we illustrate the studies by reporting data for Cr on air cleaved CdTe surfaces. These data are presented in Figure 2, where the emission from the Te 4d core level ($h\nu = 100$ eV) is shown both for the oxidised surface and following deposition of varying thicknesses of Cr. The tellurium 4d^{3/2} and 4d^{5/2} components show very pronounced satellite

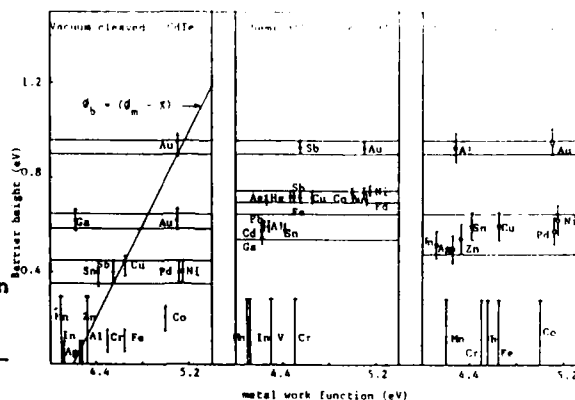


Figure 1. Plot of Schottky barrier heights against metal work functions for metals on clean, chemically etched and air-cleaved n-CdTe crystals.

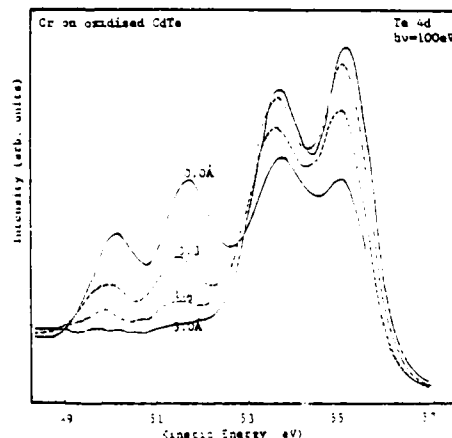


Figure 2. Flux normalised photoemission spectra of the Te 4d core level with increasing coverages of Cr. Taken at photon energy of 100 eV.

structure for photoemission from the oxidised surface. The satellite structure is shifted to larger binding energies by around 3.4 eV and arises from tellurium atoms in a TeO_2 environment.⁽³⁾ Deposition of very thin layers of Cr on the oxidised CdTe surface leads to an attenuation of the Cd 4d emission as expected. The behaviour of the Te 4d emission, however, is entirely different. Now, the component associated with TeO_2 is rapidly reduced whereas the other component first increases and subsequently decreases in intensity. The data is entirely consistent with the possibility that the TeO_2 is reduced to tellurium initially, and subsequently the tellurium is incorporated in, or on top of the metal contact.

Detailed photoemission studies of the interaction of Ag with oxidised CdTe indicated that the overlayer reduced the oxide layer to a significantly lesser extent.⁽³⁾ In the same studies, however, it has been found that Au does reduce the oxide in a manner rather analogous to the behaviour of Cr, Mn and V.

DISCUSSION

Photoelectron spectroscopy illustrates very clearly that the contacts formed between CdTe single crystal and a range of metals are not abrupt and simple. The metals illustrated in Figure 1 give rise to a range of values of ϕ_b , varying from close to zero to 0.9 eV for n-type crystals. Clearly, the data reported in Figure 1 is not consistent with the elementary model of Schottky, where a linear dependence of ϕ_b on ϕ_m is expected. The data is also quite inconsistent with models involving pinning of the Fermi level by metal induced gap states, or MIGS.⁽⁶⁾ In its most elementary form the application of this model predicts a constant value of ϕ_b of ~0.7 eV on n-type CdTe.

Photoemission studies of metal interaction with clean CdTe surfaces demonstrate that the interfaces formed are rarely abrupt. The formation of mixed phases is very common and for that reason the data of Figure 1 is probably best accounted for on the basis of defect^(7,8) and mixed phase⁽⁹⁾ models. However, the data cannot be explained on the basis of a single defect energy and requires the existence of multiple defect levels.

Clearly the interaction of many metals with oxidised CdTe surfaces lead to mixed phase contacts. Several metals lead to a drastic reduction of the oxide layer and may make intimate contact with the CdTe surface. It is thought that this is the reason why Mn, V and Cr yield similar values of ϕ_b for both clean and oxidised surfaces. Au is believed to behave in a similar manner. Ag is representative of the group of metals where the barrier

heights may be drastically influenced by the presence of the oxide layer at the interface. The surface oxide layer on chemically etched CdTe is believed to be Te rich and to lead to strong pinning of the Fermi level at approximately mid-gap. It appears that Ag may not be able to penetrate through this oxide layer so that the pinning energy remains that appropriate for the Te rich oxide rather than that for the metal overlayer. Partial reduction of the oxide may lead to a mixed phase contact where the phases present are kinetically limited. In this case non reproducible values of Schottky barrier heights are anticipated and are indeed observed.

In conclusion, metal contacts on clean cleaved CdTe surfaces lead to a wide range of Schottky barrier heights which are inconsistent with models involving metal induced gap states in their most elementary form. The range of barriers observed, and the way they are drastically influenced by oxide layers, suggest that models involving interfacial defects and mixed phases are equally, if not more important. In this complex system as well as at metal-semiconductor interfaces in general it is likely that many processes contribute to Schottky barrier formation and in certain situations one mechanism may dominate above all others. For metals on CdTe mixed phases and defects fall in this latter category.

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Abstract. The electrical properties of metal-CdTe contacts have been measured for a diverse group of 18 metals by using current-voltage and capacitance-voltage techniques. The contacts were formed by metal evaporation onto chemically etched surfaces of n-CdTe single crystals. A large number of metals yield a barrier height of 0.72 ± 0.03 V, independent of the work function of the metal. Mn, Cr and V were different, producing ohmic or very low barriers. The nature of the CdTe(110) surfaces produced by chemical etching using bromine in methanol was studied by an x-ray photo-emission technique. We have also carried out a detailed investigation into the microscopic interactions at selected interfaces by soft x-ray photo-emission using a synchrotron radiation source. Detailed comparisons of the microscopic interaction of Ag and Mn with the oxidised surfaces, using photo-emission are reported. In contrast to the behaviour of Ag, the Mn overlayer reduces completely the CdTe native oxide layer, leading to low-barrier contacts. It has been found that the bulk thermodynamic data provide an approximate description of the interface reactivity for most of the systems studied.

1. Introduction

Recently there has been an increased interest in using ultra-high vacuum-surface analytical techniques to study the microscopic structure and electronic properties of Schottky-barrier contacts to CdTe. Auger electron spectroscopy (AES) and x-ray photo electron spectroscopy (XPS) have been used to study the surfaces produced by chemical etching. In some circumstances these surfaces have been found to be severely depleted of Cd (Patterson and Williams 1978, Hage-Ali *et al* 1979, Haring *et al* 1983). In fact ellipsometry (Aspnes and Arwin 1984) and Raman scattering (Amirtharaj and Pollack 1984) measurements have shown that the surface layer following etching consists of some elemental tellurium. Using XPS and electron-loss spectroscopies, Patterson and Williams (1978), Ebina *et al* (1980) and Anthony *et al* (1982) have found TeO_2 on the surface of oxidised CdTe. In most of these studies the commonly occurring oxide, TeO_2 is observed and the other possible oxides, namely, CdO and TeO have not been unambiguously detected. The nature of the surface treatments has been shown to have strong influence on the electrical characteristics of metal-CdTe devices (Williams *et al* 1986). However, there is little understanding of Schottky barrier formation on chemically etched CdTe surfaces, and in this work we have attempted to study the macroscopic properties of metal-CdTe interfaces for a large number of metals. To investigate the microscopic interactions at these interfaces,

we have performed soft x-ray photo emission spectroscopy (SXPS) using a synchrotron radiation source for selected metals. To investigate the chemical composition of the surfaces we have used the XPS technique with a standard laboratory x-ray source. These results, together with bulk thermodynamic data, are presented and discussed in terms of various models of Schottky barrier formation.

2. Experimental

The single crystals of moderately doped n-type cadmium telluride used in this study had resistivities of approximately $10 \Omega \text{ cm}$. These crystals were grown either by the fast vertical Bridgman method or by the solvent evaporation technique. For surface preparation two different chemical etching procedures were used. The CdTe surfaces were mechanically polished to a finish of $\frac{1}{2} \mu\text{m}$ using diamond paste and they were then chemically etched in (a) a 1% bromine in methanol solution, (b) a 1% bromine in methanol solution followed by 1 mol l^{-1} KOH in methanol. The latter treatment has been found necessary to remove excess tellurium on the surface (Amirtharaj and Pollack 1984, Ferdman *et al* 1985). In order to investigate the difference between these two treatments the following control experiment was always carried out. Two samples from the same crystal were simultaneously etched in bromine-methanol following which, only one was etched in 1 mol l^{-1} KOH solution. The samples were then rinsed thoroughly and stored in methanol until they were transferred to the vacuum system. The Schottky barriers

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were fabricated by thermally evaporating a thick metal overlayer from a metal loaded tungsten filament or from a molybdenum boat at a pressure of approximately 10^{-6} mbar. The ohmic back contact was formed by annealing an In/Ga alloy for several minutes at approximately 200 °C. Except for Hg, the electrical contacts were made using air drying silver paste, and the transport properties were measured at room temperature. A liquid contact was used as the Schottky barrier in the case of mercury. The current-voltage (I - V) characteristics were measured using a Keithley 614 electrometer and a Fluke 8860A digital voltmeter. Capacitance-voltage (C - V) characteristics were measured at a frequency of 1 MHz using a Boonton C - V meter. The results presented in this paper were obtained before any appreciable aging effects occurred.

The nature of the CdTe(110) surfaces produced by chemical etching was studied by XPS using Al K α x rays of energy 1486 eV. Similar studies were carried out on clean cleaved and air cleaved CdTe(110) surfaces for comparison. The microscopic interactions between selected metals and the oxidised CdTe surface were studied using soft x ray photo electron spectroscopy (SXPS) at the synchrotron radiation source at Daresbury Laboratory, UK. The SXPS experiments were carried out in a vacuum chamber at a base pressure of $\sim 10^{-10}$ mbar. The CdTe surfaces were exposed to 100 eV photons and the photo-excited electrons were analysed using a double pass cylindrical mirror analyser. Cd 4d, Te 4d core levels and valence band spectra were recorded with increasing metal coverage on the CdTe surfaces. Metal overlayers were deposited from well outgassed tungsten filaments located about 30 cm from the sample surface. Evaporation rates were measured with a quartz crystal film thickness monitor kept at a known distance from the source. The thickness of the metal coverages were calculated by assuming that the evaporation from the filament was isotropic and well described by an inverse square law.

3. Experimental results

3.1. Transport measurements

Figure 1 shows the I - V characteristics of Pd/n-CdTe Schottky diodes which were prepared by depositing thick Pd layers onto chemically etched CdTe surfaces. The detailed form of the I - V characteristics of the diodes were found to depend on precisely how the contact was made and indeed I - V characteristics of diodes fabricated on the same crystal showed variations. Rectification factors, defined as the ratio of the forward to the reverse current, at 0.4 V varied from 10^3 to 10^5 for the three diodes shown in figure 1. Diodes 2 and 3 were prepared on the same crystal but diode 1 was made using a different crystal. This particular crystal also produced diodes with good rectifying properties for most of the other metals studied.

Forward bias I - V data were initially analysed using the conventional procedure of introducing an ideality

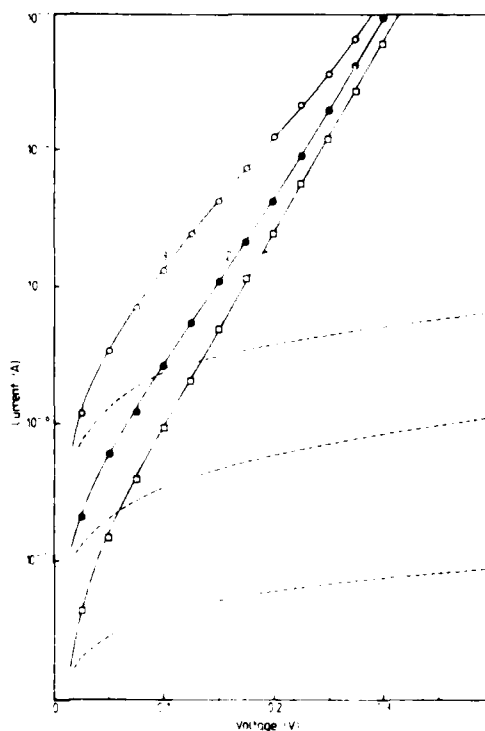


Figure 1. Forward and reverse current-voltage characteristics for three Pd/n-CdTe Schottky diodes. The points are experimental and the full lines are the calculated best fits of equation (2) through the data points. In each case the contact areas were 0.5 mm^2 .

factor n into the thermionic emission diode equation (Sze 1976, Rhoderick 1978)

$$I = I_s \exp[\beta(V - IR)/n] \quad \text{for } V > 3\beta \quad (1)$$

where $\beta = q/kT$, $I_s = SA^{**}T^2 \exp(-\beta\phi_b)$, S is the contact area, A^{**} is the modified Richardson constant, ϕ_b is the Schottky barrier height, and the other symbols have their usual meanings. The values of n and ϕ_b obtained from the gradient and the intercept of the plots of $\ln I$ versus V are listed in table 1. The ideality factors varied from 1.18 to 1.75 and the values for ϕ_b varied from 0.57 to 0.66 V. However, in view of the non ideal behaviour of the diodes these values of ϕ_b are highly unreliable. Considerable deviation of the ideality factor from unity and the excess current at the low forward bias voltage, indicates the presence of a large contribution from recombination and generation in the depletion region. Incorporating the contribution to the current which arises from recombination results in an expression of the form (Rhoderick 1978, de Sousa Pires *et al* 1985)

$$I = I_s[\exp \beta(V - IR) - 1] + I_r[\exp \beta(V - IR)^2 - 1] \quad (2)$$

Table 1. Experimentally obtained parameters for three different diodes shown in figure 1

Diode	Rectification factor at 0.4 V	(I- V) measurements				N_D (cm ⁻³)
		n	Thermionic emission (i_t)	$(i_t) + \text{recomb}$	(C- V) measurements	
			(ϕ_b) (V)	(ϕ_b) (V)	$(\phi_b)_{r,c}$ (V)	
1. Pd-CdTe	1×10^3	1.18	0.66	0.71 ± 0.02	0.71	2.8×10^{16}
2. Pd-CdTe	5×10^3	1.35	0.63	0.70 ± 0.02	0.70	3.0×10^{16}
3. Pd-CdTe	1×10^5	1.75	0.57	0.71 ± 0.02	0.77	5.8×10^{16}

By considering only mid-gap recombination centres, distributed uniformly throughout the depletion region, I_r can be expressed approximately as $I_r = Sn_iW(0)/2\tau_r$, where τ_r is the charge carrier lifetime within the depletion region, n_i is the intrinsic carrier concentration and $W(0)$ is the zero bias depletion layer width. In equation (2), the first and second terms represent the pure thermionic emission and recombination contributions respectively. This current-voltage relation was used to analyse the forward I - V characteristics of the diodes instead of equation (1). More accurate estimates of the Schottky barrier heights were obtained using a curve fitting procedure based on equation (2) and this has been discussed in detail elsewhere (McLean *et al* 1986). Barrier heights (ϕ_b) obtained using this procedure are also presented in table 1. It is relevant to note that the method produces almost the same barrier height of ~0.71 V for all three diodes, although their current-voltage characteristics are quite different.

When the capacitance-voltage data were analysed by plotting capacitance² against reverse voltage, good straight lines were obtained up to about 1.0 V for all diodes fabricated. Barrier heights (ϕ_b)_{*r*} and ionised donor concentrations (N_D) were obtained from the intercept and the gradient, following the conventional procedure (e.g. Sze 1976, Rhoderick 1978). A few diodes contained a high density of electron traps in the surface layer leading to large errors in the determination of ϕ_b from the

capacitance method. An analysis of these has not been included in this paper. The C - V characteristics for the diodes for which I - V data were shown in figure 1 are presented in figure 2. These produce a value in the range 0.70–0.77 V for barrier height showing a close agreement with values obtained from the curve fitting procedure.

Although the Schottky barriers extracted from the analysis are the same, the forward I - V characteristics of diodes on different crystals vary due to different contributions from recombination and generation. This can arise from bulk defects in the crystal or from surface imperfections created during chemical etching. One particular crystal, grown using the solvent evaporation method, always showed a small recombination contribution indicating a low density of bulk defects. Most of the results reported here have been obtained using this crystal. Defects or traps reduce the lifetime (τ) of charge carriers, and hence increase the recombination current. For a good quality crystal, τ has a higher value and therefore the recombination contribution is small. Diodes on these crystals exhibit nearly ideal behaviour with n values close to unity. However, if the density of recombination centres is large, the recombination can be quite considerable and this process can dominate the conduction. In these cases diodes exhibit n values very close to 2.0 (e.g. Shockly and Read 1952, Hall 1952, Sah *et al* 1957, Yu and Snow 1968).

The barrier heights extracted for a number of metals deposited on chemically etched CdTe crystals are presented in table 2; these have been derived from I - V and C - V methods. Several points are immediately clear:

(a) There is a group of metals (Ni, Co, Sb, Fe, and Pd) which yield values of ϕ_b in the range 0.60 to 0.77 eV, having similar values when derived from I - V and C - V techniques.

(b) Another group (Au, Ag, Hg) yield values of ϕ_b ~ 0.72 V as determined from I - V characteristics but substantially higher barriers extracted from the capacitance method.

(c) A third group of metals (Cd, Zn, Sn, Pb, Ga, Al) yield lower values of ϕ_b deduced from transport studies. Furthermore the barriers measured for this group are highly irreproducible. The barrier determined by C - V for Pb is unrealistically large.

(d) A group of metals (Cr, Mn, V) yield barriers so small that they are essentially ohmic (i.e. bulk limited conduction) and cannot be measured.

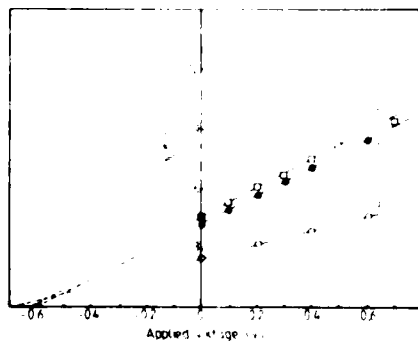
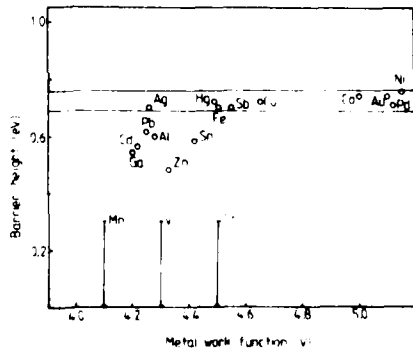
**Figure 2.** The capacitance² versus reverse voltage characteristics measured at 1 MHz for the same diodes of figure 1

Table 2. Schottky-barrier parameters for various metals on chemically etched n-CdTe as measured by $I-V$ and $C-V$ methods.

(I-V) measurements					
Thermionic emission (TE)			(TE) + recomb.	(C-V) measurements	
Metal	<i>n</i>	(<i>ϕ_b</i>) (V)	(<i>ϕ_b</i>) (V)	(<i>ϕ_b</i>) _{C-V} (V)	<i>N_D</i> (cm ⁻³)
Au	1.52	0.63	0.74	1.20	3.0 · 10 ¹⁶
Ag	1.19	0.63	0.70	0.88	2.5 · 10 ¹⁶
Hg	1.30	0.66	0.72	1.01	4.3 · 10 ¹⁶
Cu	1.30	0.69	0.72	—	—
Ni	1.07	0.74	0.77	0.76	3.0 · 10 ¹⁷
Co	1.68	0.60	0.74	0.74	1.2 · 10 ¹⁶
Sb	1.17	0.66	0.70	0.69	1.1 · 10 ¹⁷
Fe	1.05	0.67	0.69	0.72	1 · 10 ¹⁶
Pd	1.18	0.66	0.71	0.71	2.8 · 10 ¹⁶
Cd	—	—	0.56	—	—
Zn	1.41	0.46	0.48	0.48	1.1 · 10 ¹⁶
Sn	1.31	0.55	0.57	0.59	5.2 · 10 ¹⁶
Pb	1.05	0.60	0.62	1.36	—
Ga	1.03	0.53	0.54	0.63	2.0 · 10 ¹⁶
Al	1.05	0.60	0.61	—	—
Cr	} Ohmic or low barriers: <i>ϕ_B</i> ≈ 0.3 V				
Mn					
V					

The results presented here are quite different from those presented by Ponpon and Siffert (1977). These authors reported barrier heights in the range 0.68 to 0.89 V for a range of metals on chemically etched n-CdTe, determined by the photoresponse and $I-V$ methods. It was reported that the barrier heights were related to the work function of the metals via the linear relationship $\phi_b = 0.154\phi_m - 0.106$. This relationship is not observed in these studies (figure 3). It should be pointed out that crystals etched with the 1 mol l⁻¹ KOH in methanol solution produced barriers similar in magnitudes to those etched using only the 1% bromine in methanol solution. However, the former diodes in general showed improved rectification factors and good reverse current characteristics.

**Figure 3.** Plot of barrier heights versus metal work functions for various metals on chemically etched CdTe surface.

Finally an important point should be made relating to measured barriers for Au and Sb on n-CdTe. Most diodes yield the $I-V$ barrier heights given in table 2 but in several cases the value of ϕ_b extracted from the transport measurements was 0.93 V, i.e. considerably higher. In measurements carried out on a large number of diodes no values of ϕ_b in between 0.74 and 0.93 V have been observed for these two contact materials. The high value of 0.93 V has also been observed for Cd-Au alloy (Kuech 1981), for Al and Au (Patterson and Williams 1982) and for Ni (So *et al* 1985). Detailed aspects of these results are under investigation.

3.2. Surface analysis by xps

The xps spectra obtained for clean cleaved, air cleaved and chemically etched CdTe(110) surfaces, using Al K α (1486 eV) radiation are shown in figure 4. The most prominent features of the spectra are the Cd 3d emission at ~ 405 eV and the Te 3d emission at ~ 580 eV. The spin-orbit splittings $3d_{5/2}$ and $3d_{3/2}$ are also seen for both elements. The spectra for air cleaved and chemically etched CdTe reveals the presence of C and O on these surfaces. The chemical shifts in the Te 3d peaks in these two cases are due to the presence of TeO₂ on the surface (Humphreys *et al* 1980). These shifts are clearly shown in the inset of figure 4(b, c). Similar chemical shifts are not observed on the Cd 3d core level emission. We have also studied the stoichiometry of the oxidised surfaces using the relative intensities of the Cd and the Te 3d emission. Comparison of the Te 3d emission intensity (oxidised + unoxidised) with the Cd 3d emission intensity for oxidised and clean surfaces reveals that the air cleaved surfaces are stoichiometric and the chemically etched surfaces are slightly enriched in tellurium.

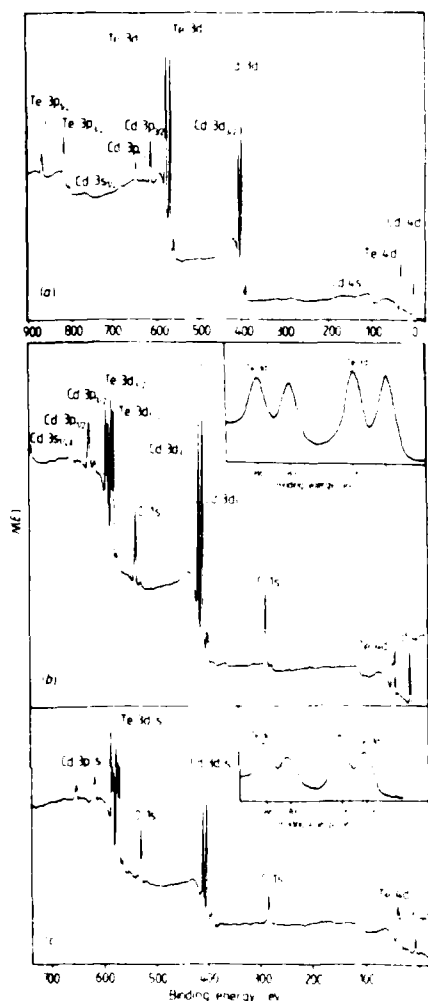


Figure 4. X-ray (Al K α , 1486 eV) induced photoelectron spectra of (110) surfaces of CdTe: (a), cleaved in an ultra high vacuum of $\sim 10^{-10}$ Torr; (b), exposed to air for 48 h and (c), etched in 50% bromine in methanol solution.

3.3. Soft x-ray photo-emission spectroscopy

In the investigations of microscopic interface reactions two cases, namely Ag and Mn representing high and low barrier situations on etched n-CdTe, have been studied. In figure 5 we show SXPS spectra ($h\nu = 100$ eV) corresponding to the Te 4d and Cd 4d core level emission respectively for the etched CdTe surface and following deposition of increasing amounts of Mn. Firstly, consider the lineshapes for zero Mn coverage. The spin-orbit split Te 4d_{5/2} and 4d_{3/2} emission also have a satellite at around 4 eV to higher binding energy, clearly shown in figure 5.

This emission has been previously shown to originate from tellurium atoms in TeO₂ on the CdTe surface (Humphreys *et al* 1980). The relative amplitudes of the oxidised and unoxidised Te components enable the thickness of the oxide to be estimated; in figure 5 this is equivalent to a thickness of ~ 1 Å. Furthermore, comparison of the Te 4d emission intensity (oxidised + unoxidised) with the Cd 4d emission for etched and clean cleaved surfaces enable the stoichiometry of the surface region to be estimated. These studies demonstrated that the chemically etched surfaces are close to stoichiometric in Cd and Te, but with a slight excess of Te.

Deposition of Mn onto the chemically etched surface leads to dramatic changes in the SXPS spectra of figure 5. First of all the Cd 4d emission is attenuated quite rapidly and a chemically shifted component appears at lower binding energies (higher kinetic energies). This behaviour is also seen when Mn is deposited on atomically clean cleaved CdTe and clearly corresponds to a surface dissociation of cadmium telluride. The Te 4d emission is influenced in a very different way. First, the TeO₂ component is reduced and ultimately removed and at the same time the unoxidised tellurium component of the emission increases. Clearly, this is due to a reduction of tellurium oxide. For Mn coverages larger than those shown in figure 5 there is a slow reduction of the Te 4d emission intensity as the Mn overlayer attenuates substrate emission. This reduction of the TeO₂ is observed for thick oxide layers on air oxidised surfaces also, as illustrated in figure 6. Here the surface is heavily oxidised and the oxide layer is estimated to have a thickness of around 3 Å. It may be seen that as the oxide is reduced, the unoxidised Te 4d component first increases in intensity and subsequently decreases.

These investigations clearly show that complex microscopic interactions occur between the Mn and the chemically etched CdTe surface. Manganese interacts with clean CdTe to form manganese telluride and/or cadmium manganese telluride (Cd,Mn Te). Furthermore, for the etched surface the manganese reduces the TeO₂ forming manganese oxide (probably Mn₂O₃) and manganese telluride. At this stage it is not possible to extract further details relating to these reactions from the data presented here.

We now consider the case of Ag on an oxidised CdTe where SXPS data are shown in figure 7 with increasing Ag thickness. Here the Cd 4d emission is attenuated somewhat more rapidly, but the Te 4d emission remains almost unaffected. In addition even for an Ag coverage of 13 Å the oxide is not fully reduced. The fact that the Cd 4d emission is attenuated more rapidly than the Te 4d component is not due to differences in escape depths. The Te 4d electrons emerge with kinetic energies in the range 48–55 eV and electrons with these energies should be more surface sensitive than those associated with the Cd 4d levels where the kinetic energies are higher. A possible interpretation of the data of figure 7 is that the Ag forms clusters with nucleation of these being preferentially on Cd rich regions of the surface. For this to be so it is necessary to assume a non uniform surface with regions

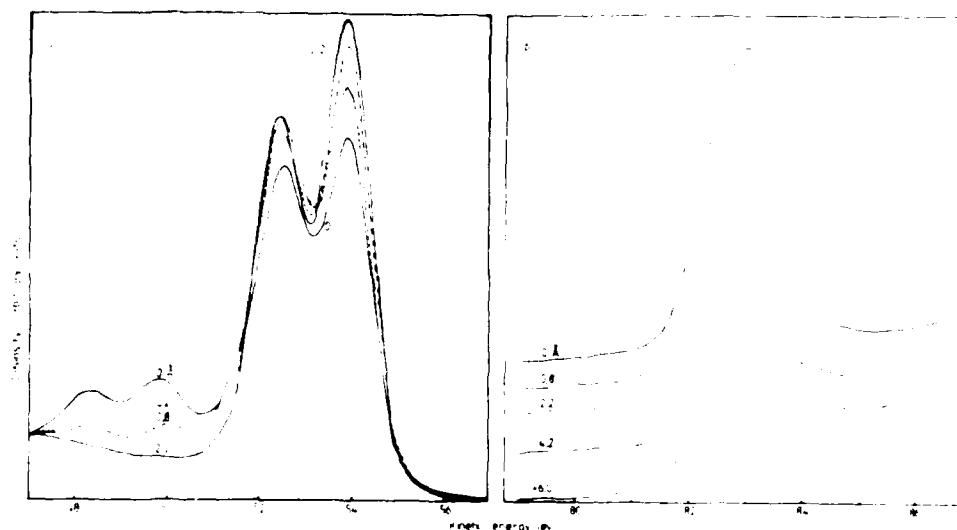


Figure 5. Soft x-ray photo-emission spectra of (a) Te 4d and (b) Cd 4d core levels measured from a chemically etched CdTe surface with increasing coverages of Mn (shown on the curves in Å). Spectra were taken at a photon energy of 100 eV and normalised to incident photon flux.

rich in Cd (or CdO) and other regions rich in Te and TeO_2 . An alternative possibility is that Ag forms clusters and that excess Te diffuses out through the Ag overlayer. Provided the oxidised CdTe surface is uniform it is this latter case that is the most likely. Chemical shifts associated with the Cd 4d emission are not observed in this case.

4 Discussion

The chemical nature of the CdTe surfaces is clear from our XPS and SXPS studies. Vacuum cleaved surfaces are

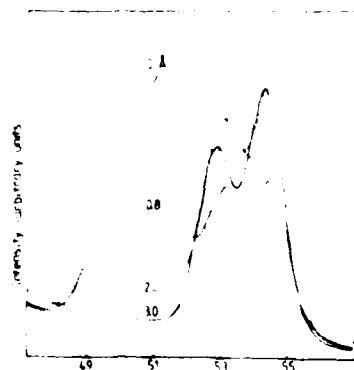


Figure 6. Soft x-ray photo-emission spectra of Te 4d core level measured from a heavily oxidised air cleaved CdTe surface with increasing coverages of Mn (in Å). Spectra were taken at a photon energy of 100 eV and normalised to incident photon flux.

stoichiometric in Cd and Te, with no oxidation of the surface. Both air cleaved and bromine-methanol etched surfaces have TeO_2 as a constituent of the surface layer. The thickness of the oxide layer varies in the range (1–3) Å depending on the degree of oxidation. The nature of the possible oxides of Cd, however, cannot be extracted from the data presented here. Air cleaved CdTe surfaces are stoichiometric in Cd and Te, but the chemically etched surfaces are slightly enriched in Te. The enthalpies of formation of the compounds TeBr_2 and CdBr_2 show that the bond strengths of Br to Te and Cd are approximately 2.2 and 3.4 eV respectively (Aspnes and Arwin 1984). Thus bromine should react much more readily with Cd than with Te. Depending on relative solubilities and rates of reaction, these different bond strengths suggest that any surface residue after bromine-methanol etching should primarily be Te. Analysis of the etchant solution confirms this by showing a higher concentration of Cd than Te in solution (Haring *et al.* 1983). The thickness of this Te-rich layer has also been estimated using various techniques. These values vary up to 40 Å depending on the strength of the bromine-methanol used and the length of time of chemical treatment. For ~1% bromine in methanol solution the estimated thickness is less than 10 Å (Feldmann *et al.* 1985).

In order to gain an understanding of the interactions between the evaporated metals and the chemically etched CdTe surface it is desirable to examine thermodynamical aspects of the oxide stability. It should be noted, however, that bulk thermodynamic data of oxide stability will probably serve as no more than a guide to understanding surface and interface reactions where kinetic effects, surface and interface energies may play a significant role.

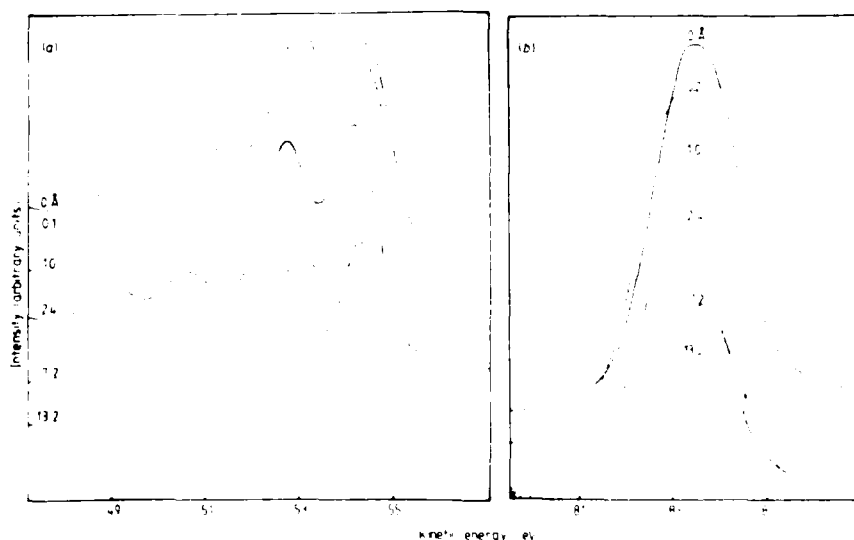


Figure 7. Flux normalised photo-emission spectra of (a) Te 4d and (b) Cd 4d core levels with increasing coverages of Ag (in Å) taken at a photon energy of 100 eV

in the formation of various phases. In table 3 we present the heats of formation ΔH^0 of a range of commonly occurring oxides taken from the *Handbook of Chemistry and Physics* (1977). ΔH^0 is defined by the equation

$$xM + \frac{y}{2} O_2 \rightarrow M_xO_y + \Delta H^0$$

where M refers to the metal. A large negative value of ΔH^0 indicates a strongly exothermic reaction with the formation of a stable oxide. It can be seen in table 3 that the oxide stability increases as one progresses from Au to V. Therefore it is anticipated that V, Al, Mn, and Cr would form more stable oxides than either Cd or Te and may therefore be expected to reduce the oxide layer on CdTe. This, however, is not expected for Au, Ag, Hg, Ir and Cu. Studies of microscopic interactions outlined in the previous section are in good agreement with this view for the cases of Mn and Ag (Dharmadasa *et al* 1986a, b). Recent studies have shown that Cr also reduces the oxide on CdTe and also demonstrate that the situation for Au is more complex than predicted in table 3, with considerable outdiffusion of tellurium occurring. This will be considered in detail elsewhere (Dharmadasa and Williams 1987).

Table 4 shows the heats of formation of a range of metal tellurides, ΔH_f^0 , as well as the heat of solution ΔH_s^0 for infinite dilution for Cd dissolved in liquid metals. These were obtained from Mills (1974) and Niessen *et al* (1983). Metals with smaller negative values of ΔH_f^0 are expected to form tellurides which are less stable than CdTe whereas metals such as Mn are anticipated to react with CdTe to form the appropriate telluride, as observed. Unfortunately the appropriate data for Cr and V tellurides were unobtainable and are therefore not included in the table.

Finally, it should be pointed out that metals with negative values of ΔH_f^0 are anticipated to form stable alloys with Cd, and Pd, Au, Ag and Sb fall into this category. The formation of Au-Cd and Ag-Cd alloys mean that tellurium is released at the interface and appears to diffuse out through the gold and silver overlayers. This conclusion was also arrived at by Bassol *et al* (1985) using Auger depth profiling.

Our previous studies have shown that the metals on clean CdTe surfaces lead to a wide range of Schottky barrier heights. Cr, V and Mn producing close to zero barriers and Au producing very high barriers. For the case of chemically etched CdTe surfaces three different groups of metals are observed:

(i) Highly reactive Cr, Mn and V reduce the surface oxide completely, react with the underlying Te rich (or Cd deficient) layer and gain access to bulk CdTe. These metals therefore produce barriers very similar to those on clean CdTe surfaces.

(ii) Unreactive metals (Au, Ag, Hg, Cu, Ni, Co, Sb, Fe and Pd) as predicted by heat of formation of tellurides are completely decoupled from CdTe by the interfacial layer and yield a constant barrier height of 0.72 ± 0.03 V. The existence of TeO₂ at the interface is reflected in C 1s measurements. This technique produces excessively large barrier heights which are characteristic of MIS structures (Rhoderick 1978) with Au, Ag, Hg and Cu. These metals do not reduce the TeO₂ present on the surface. Other metals consume the surface TeO₂ and give rise to barrier heights in agreement with I-V technique.

(iii) A group in between (Cd, Zn, Ga, Al, Sn and Pb) produce lower barrier heights than 0.7 V with a poor reproducibility. These metals partly react with the

Table 3. Heat of formation (ΔH°) values of inorganic oxides from the *Handbook of Physics and Chemistry* (1977).

Metal	Possible oxides	ΔH° (kJ mol ⁻¹)
Au	Au ₂ O ₃	- 8.8
Ag	Ag ₂ O	- 31.8
	Ag ₂ O ₂	- 28.2
Hg	Hg ₂ O	- 93.5
	HgO	- 91.7
Ir	IrO ₂	- 165.8
Cu	Cu ₂ O	- 171.1
	CuO	- 158.8
Ni	NiO	- 241.7
Cd	CdO	- 261.1
Te	TeO ₂	- 328.1
Zn	ZnO	- 356.3
Bi	Bi ₂ O ₃	- 583.9
	BiO	- 211.7
Sn	SnO ₂	- 596.2
	SnO	- 287.5
Mg	MgO ₂	- 631.5
	MgO	- 605.0
As	As ₂ O ₃	- 650.9
Pb	Pb ₂ O ₄	- 733.8
	PbO ₂	- 276.9
	PbO	- 222.3
Co	Co ₂ O ₄	- 874.9
	CoO	- 239.9
Sb	Sb ₂ O ₄	- 874.9
	Sb ₂ O ₃	- 710.9
Ga	Ga ₂ O ₃	- 1076.0
	Ga ₂ O	- 340.5
In	In ₂ O ₃	- 926.1
Fe	Fe ₃ O ₄	- 1127.2
	Fe ₂ O ₃	- 841.4
Cr	Cr ₂ O ₃	- 1153.7
	CrO ₂	- 598.0
	CrO ₃	- 594.5
Mn	Mn ₂ O ₄	- 1395.3
	Mn ₂ O ₃	- 968.4
	MnO ₂	- 531.0
	MnO	- 388.1
Al	Al ₂ O ₃	- 1873.4
	Al ₂ O	- 132.3
P	P ₄ O ₁₀	- 2988.2
V	V ₅ O ₁₀	- 4521.1
	V ₂ O ₅	- 1603.5
	V ₂ O ₄	- 1439.4
	V ₂ O ₃	- 1259.5
	VO	- 425.1

intermediate layer and do not completely decouple the metal from CdTe. The degree of reaction is determined by kinetic considerations and the thickness of the oxide layer present on the surface, and is therefore difficult to control.

Most metals on chemically etched CdTe surfaces produce diodes with good rectification properties. Their non-ideal behaviour can be explained in terms of recombination and generation at the interface and the presence of the native oxide layer on the surface. Recombination and generation arise mainly due to bulk defects and the imperfections created by chemical etching. The constant barrier height of ~ 0.72 V observed for most of the non reactive metals suggest a strong Fermi level

Table 4. Heat of formation for metal tellurides and heat of solution at infinite dilution for liquid Cd solved in liquid metals.

Metal	Metal-telluride	ΔH_f° (kJ mol ⁻¹)	ΔH_s° (kJ mol ⁻¹)
Au	AuTe ₂	18.6	41
Ag	Ag ₂ Te	36.0	9
Hg	HgTe	31.8	2
Cu	CuTe	41.8	3
Ni	NiTe ₂	- 88.0	9
Co	CoTe _{1.21}	38.0	28
Sb	Sb ₂ Te ₃	56.5	8
Fe	FeTe ₂	72.4	77
Pd	PdTe ₂	54.0	104
Cd	CdTe	100.8	0
Zn	ZnTe	119.2	4
Sn	SnTe	62.0	1
Pb	PbTe	68.6	5
Ga	Ga ₂ Te ₃	274.9	3
Al	Al ₂ Te ₃	318.8	14
Cr	—	—	81
Mn	MnTe ₂	126.0	10
V	—	—	42

ΔH_f° = heat of formation at 298 K for metal tellurides

ΔH_s° = heat of solution at infinite dilution for liquid Cd solved in liquid metals

pinning at the gap centre, 0.72 ± 0.03 V below the conduction band minimum. On the basis of these results we suggest that this strong pinning is due to the states created by the Te rich (or Cd deficient) surface layer. The contacts made to this Te-rich outer layer, with a metal, semiconductor or an electrolyte will not alter this fixed barrier height unless they react with the outer layer on the surface. The observation of a 0.79 V barrier height for an InSb-CdTe heterojunction (Rabin *et al.* 1980) is a good example. Their CdTe surface was prepared by etching in a 12% bromine-methanol solution prior to deposition of InSb and therefore the barrier is determined by the Te rich layer. A large number of electrolytes on etched n-CdTe surfaces have also shown a Fermi level pinning around 0.7 V below the conduction band (Tanaka *et al.* 1981).

The identification of the mechanisms governing Schottky barrier formation is of great general interest and the relevant mechanisms are not well understood. Clearly the metal-CdTe interfaces described in this work are complex on a microscopic scale and it may be anticipated that the data cannot be accounted for in terms of any single simple mechanism. Nevertheless it is of interest to examine the applicability of some of the most relevant models. It is known that a Te rich layer exists at interfaces with several metals. Following Freeouf and Woodall (1981), if it is assumed that the relevant work function is that of Te ($\phi_{Te} = 5.00$ eV, Sze 1976) and taking a value of 4.28 eV for the electron affinity of CdTe (Zanio 1987), one obtains a value of 0.72 V for the barrier height for Te on CdTe. This is in remarkable agreement with the value of ϕ_b observed in this work for the range of metals that do not react with the Te rich surface layer. However, it should also be noted that the metal induced gap states

model (Flores *et al* 1977, Tersoff 1984a, b, 1986) and disorder-induced gap states model (Hasegawa *et al* 1986) also predict values of ϕ_b of around 0.7 V, and clearly these models cannot easily be discounted. The fact that metals such as aluminium yield low barriers on clean surfaces but high barriers on etched surfaces indicates that the effective work function model is more appropriate than the latter ones. Another popular and much discussed model of Schottky barrier formation is the defect model where simple defects such as vacancies and anti-site defects in the semiconductor at the interface pin the Fermi level. Clearly, for metals on etched CdTe, the interfaces are of poor quality and deficient in Cd and it is quite likely that defects will play an important role. However, at this stage, it is difficult to deduce any quantitative information relating to the role of defects in the metal–CdTe system. It is of importance to note the observation of two distinct barrier heights for Au and Sb on etched CdTe. The observations that Au and Sb can each give two well defined barrier heights (0.72 and 0.93 V) is most easily explained in terms of the defect model and it is difficult to see how this observation can be accounted for on the basis of metal-induced gap states. However, it is possible that the observation is also as a result of chemical effects associated with the amount of excess Te at the interface.

Acknowledgments

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AN INVESTIGATION OF METAL CONTACTS TO II-VI
COMPOUNDS: CdTe AND CdS

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ABSTRACT

Extensive investigations have been made of metal interfaces to single crystal CdS and CdTe. This is part of a programme aimed at understanding the behaviour of a CdS:CdTe solar cell and improving its efficiency and lifetime. Schottky barrier heights have been investigated for a large number of metals on both clean and oxidised surfaces. Parallel studies of microscopic interactions at the interfaces have been carried out using a range of surface science techniques particularly photoemission. A wide range of barrier heights have been observed for different metals on CdS and CdTe and the behaviour of the two semiconductors is very similar. Conventional theories taken individually are unable to fully account for the data, but the range of barriers observed and the way they are influenced by the method of fabrication suggests that models involving interfacial defects and mixed phases are most important for these two semiconductors.

INTRODUCTION

Electrical contacts to II-VI semiconductors are of importance in a number of applications such as solar cells, infra red detectors and light emitting devices. Contacts to semiconductors such as CdS and CdTe are also of interest from a fundamental point of view in that they are an important test of the linear theory of Schottky barrier formation. The linear theory¹ relates the barrier height, ϕ_b to the metal work function, ϕ_m for a metal on an n-type semiconductor according to the formula

$$\phi_b = S(\phi_m - \chi_{sc}) + C$$

where C is a constant and χ_{sc} is the electron affinity of the semiconductor. Sometimes the electronegativity, χ_m of the metal is used in preference to the work function. It has also been reported that the quantity S, referred to as the "index of interface behaviour", is small for metals on covalent semiconductors such as Si but large on the more ionic semiconductors, and that a well defined covalent-ionic transition exists¹. It was reported that the metals on CdS lead to a value of S of about 0.6, i.e. on the "ionic-covalent transition" boundary¹. At the same time the value of S for CdTe was reported to be small (~0.3). In previous work we have questioned the assertion that S is small (or even meaningful) for metals on CdTe, and furthermore we have shown that the measured values of ϕ_b are highly sensitive to the nature of the CdTe surface when the metal contact is deposited².

In this paper we consider more detailed aspects of the nature of the surface and interface on Schottky barriers formed to CdTe and we have extended these studies to the semiconductor CdS in

view of its most important location in the so called "ionic-covalent transition" interpretation of the linear model.

EXPERIMENTAL

Schottky barrier heights were established for metals on n-type CdTe and CdS by current-voltage and capacitance-voltage methods as discussed elsewhere^{3,4}. Metals were deposited by evaporation from a tungsten filament or molybdenum boat as appropriate. In some instances the metals were deposited on atomically clean surfaces prepared by cleavage in ultra-high vacuum. In addition metals were deposited on surfaces cleaved and chemically etched, or cleaved in the atmosphere.

The nature of the semiconductor surfaces and the detailed microscopic interactions with metals were probed using photoelectron and Auger electron spectroscopies. This was achieved using a double pass cylindrical mirror analyser and light from the synchrotron storage ring (SRS) at Daresbury Laboratory. Full details of the experimental approach have been presented elsewhere⁵.

The CdS and CdTe crystals had carrier densities of typically 10^{16}cm^{-3} . All experimental measurements were made with the samples at room temperature. The ohmic back contacts were made using an In:Ga eutectic.

RESULTS

In Figure 1 we present typical I-V characteristics for silver on clean cleaved and air cleaved CdS crystals. Silver has been chosen as an example which yields particularly good diode

behaviour. For the Ag on clean CdS case an analysis using thermionic emission theory is adequate and yields a value of 0.78eV for the Schottky barrier height and an ideality factor of around 1.05. The rectification factor is also excellent. With increasing time the characteristics become non-ideal with the forward current decreasing, as shown in Figure 1(a). This suggests that some kind of interdiffusion process or chemical reaction may take place at the Ag-CdS interface which leads to non-ideal diodes.

Figure 1(b) also shows the I-V characteristics of the diodes formed by depositing Ag on air cleaved CdS. In this case the apparent barrier height is substantially smaller (0.52eV) and the reverse current is correspondingly large. These diodes also show appreciable time dependence with ϕ_b increasing to around 0.70eV after several months. It was also found that heating the contact as well as slower deposition rates of the metal contact also led to the higher values of ϕ_b .

It is quite clear that the Schottky barrier heights for Ag on n-type CdS are quite dependent on the detailed nature of the metal-CdS interface and indeed this was found to be the case for a number of other metals. The barrier heights for a range of metals on air cleaved CdS are presented in Figure 2(a) together with an indication of the effect of ageing. It is evident from this plot that the linear model referred to earlier is entirely inappropriate and although the barrier heights do cover a large energy range of about 1eV the derivation of a single value for S from the data is clearly inappropriate. Our results for metals on clean CdS appear to fully confirm this view.

Studies of metal contacts to CdTe crystals are very much in accord with the data presented above for metals on CdS. Figure 2 also shows Schottky barrier heights for metals on clean and chemically etched n-type CdTe single crystals. A few points are

immediately apparent. Firstly, the values of ϕ_b are highly dependent on the nature of the metal-CdTe surface and, secondly, the linear model is again clearly inappropriate. Also, an important point should be made relating to the barriers measured for Au and Sb on n-CdTe. These contacts yield either 0.74eV or 0.93eV barriers with chemically etched surfaces and 0.60eV or 0.93eV on the clean surface. In measurements carried out on a large number of diodes no values of ϕ_b in between the above values have been observed. Time dependent effects are also observed for metal contacts on CdTe.

The transport studies strongly suggest that complex interactions occur at the interfaces between metals and CdS and CdTe. The photoemission studies fully bear this out and to illustrate this we present, in Figure 3, the case of manganese on CdTe clean and oxidised surfaces.

The upper panel of Figure 3 shows the Te 4d and Cd 4d shallow core level spectra as a function of increasing Mn coverage on the clean, cleaved CdTe surface. These were recorded at a photon energy of 100eV, in order to achieve high surface sensitivity. The Cd 4d peak undergoes a gradual attenuation while the Te 4d emission remains strong as increasing amounts of Mn are deposited. A chemically shifted Cd 4d component appears about 0.9eV towards the lower binding energy side at higher coverages, and this peak corresponds to Cd dissociated from CdTe. This data clearly indicates the disruption of the clean CdTe surface as a result of formation of tellurides of manganese releasing metallically bonded Cd at the interface.

The lower panel of Figure 4 shows similar data for Mn on the air oxidised CdTe surface. The spin orbit split Te 4d_{5/2} and 4d_{3/2} emission for the oxidised surface also has an additional doublet at about 3.4eV to higher binding energy. This emission originates from tellurium atoms in TeO₂ on the CdTe surface.

Deposition of Mn onto these surfaces leads to dramatic changes in the SXPS spectra. The Cd 4d emission is attenuated quite rapidly, similar to that of Mn on the clean CdTe surface. However, the Te 4d emission is influenced in a completely different way. Firstly, the TeO_2 component is reduced and ultimately removed and at the same time the unoxidised tellurium component of the emission increases. Clearly, this is due to a reduction of tellurium oxide. For larger Mn coverages there is a slow reduction of the Te 4d emission intensity as the Mn overlayer attenuates substrate emission.

The Mn-CdTe system was selected as an example to illustrate the microscopic interactions at these interfaces. We have also studied several metals (Cr, Ag and Au) on both clean and oxidised CdTe surfaces, and most metals behave in a similar way. Strong out-diffusion of Te and reduction of surface oxides are commonly seen in these systems. We expect that similar behaviour will occur for metals on CdS, and this is now being studied in detail.

DISCUSSION

It can be seen from the results presented above that there are some clear similarities between the behaviour of metals on the CdS and CdTe surfaces. Metal contacts to both semiconductors exhibit a wide range of barrier heights (of about 1 eV in both cases) and these barrier heights show a considerable dependence on the nature of the semiconductor surface. For example, a thin oxide layer can change dramatically the barrier heights obtained for a metal on either CdS or CdTe. Also ageing effects are seen for Schottky barriers to both semiconductors which, depending on the particular system, show a change in the barrier height as well as in generation-recombination effects or other non-ideal behaviour.

It can be seen from Figure 2 that the linear model does not seem to adequately describe the variation of Schottky barrier heights for metals on CdS and CdTe. Linear behaviour is not seen even if electronegativity values are substituted for the work function of the metals. It therefore appears that the "index of interface behaviour", S is not a useful parameter for Schottky barriers to CdS and CdTe.

There has been a great deal of discussion recently about the importance of the metal-induced gap states (MIGS) model at metal-semiconductor interfaces⁶. This model suggests that, for an intimate contact between metal and semiconductor the metal wave functions are not abruptly terminated at the junction but extend far enough into the semiconductor to create interface states in its forbidden band gap. These states pin the Fermi level at a particular energy in the band gap which should be constant for a given semiconductor with a high density of induced states. Since the MIGS model requires one single pinning level for each semiconductor it cannot be significant in the case of CdS or CdTe where a wide range of barrier heights are seen. The two values of barrier heights for the same metal-semiconductor system, as observed for Au and Sb on CdTe clearly cannot be explained by this model.

Another model which has attracted much interest in Schottky barrier theory is the defect model⁷. This model suggests that if a large enough number of defects is created at the metal-semiconductor interface then these defects will act as surface states in the band gap and may pin the Fermi level. The interface defects might be caused by a number of phenomena, for example a highly stepped surface, disorder at the interface, a thin oxide layer, or a chemical reaction or diffusion between the metal and semiconductor. If any of these create a density of gap defect states of the order of 10^{14} states/cm⁻² then the position of the

Fermi level may be relatively independent of the metal work function.

Extensive work investigating the metal-CdTe interface has revealed that the majority of metals either react with CdTe or diffuse into the semiconductor^{3, 6}. Some similar work has been carried out for the metal CdS interface which appears to behave similarly⁹⁻¹³. Clearly several different defect levels would be required to account for the experimental data for metals on CdTe and CdS, and this may indeed be feasible in view of the complex reactions which take place. The ageing effects are probably associated with the time dependence of the reactions and interdiffusion mechanisms. Also observation of two discrete values of ϕ_b for certain metal-CdTe systems can be easily explained in terms of the defect model.

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FIGURE CAPTIONS

Figure 1. Forward and reverse I-V characteristics for Ag/CdS diodes fabricated on (a) clean cleaved and (b) air-cleaved CdS surfaces. Open circles (o) and full circles (●) indicate characteristics for contacts as made and about 2 months old respectively. In each case the contact areas were 0.2mm^2 .

Figure 2. Plot of Schottky barrier heights against metal work functions for metals on (a) air cleaved n-CdS, (b) clean n-CdTe and (c) Bromine-Methanol etched n-CdTe.

Figure 3. Soft-X-ray Photoemission spectra of the Te 4d and Cd 4d core levels from (a) clean CdTe and (b) oxidised CdTe surfaces with increasing coverages of Mn. Spectra were taken at a photon energy of 100eV and normalized to incident photon flux.

FIGURE 1

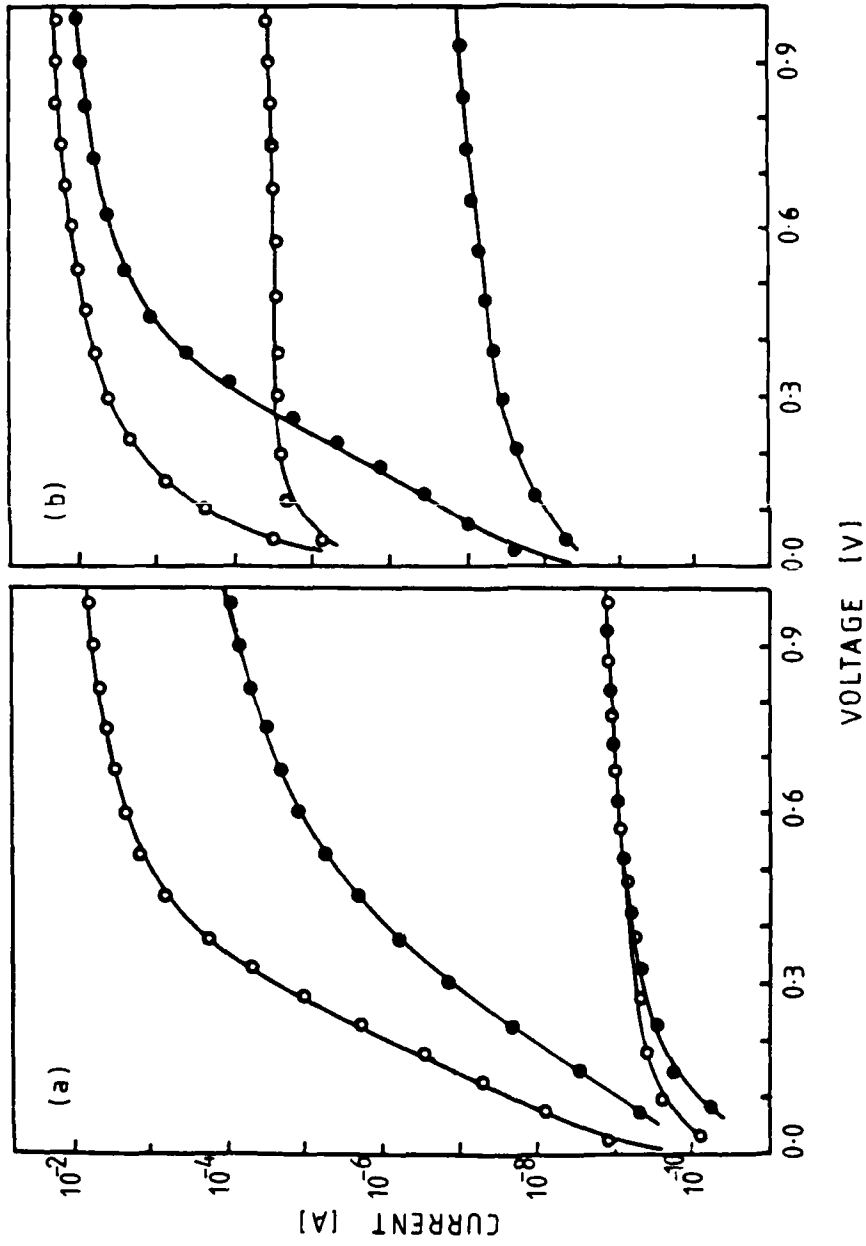


FIGURE 2

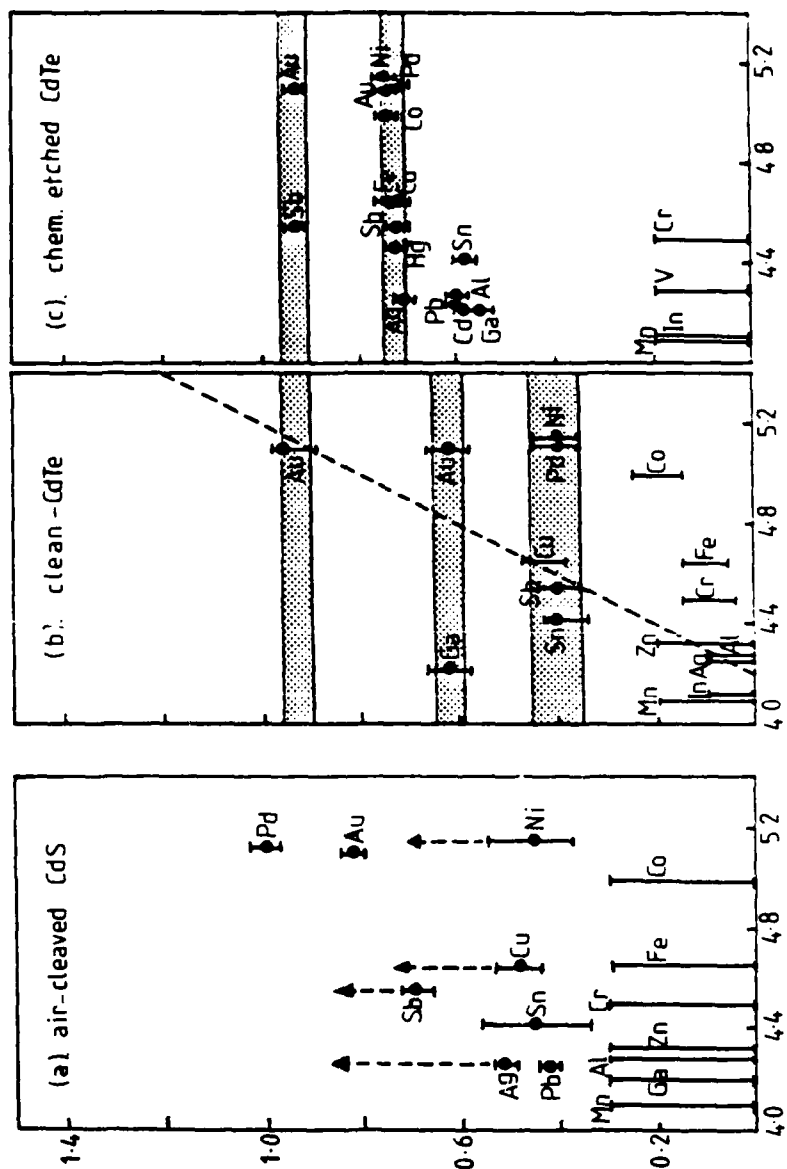
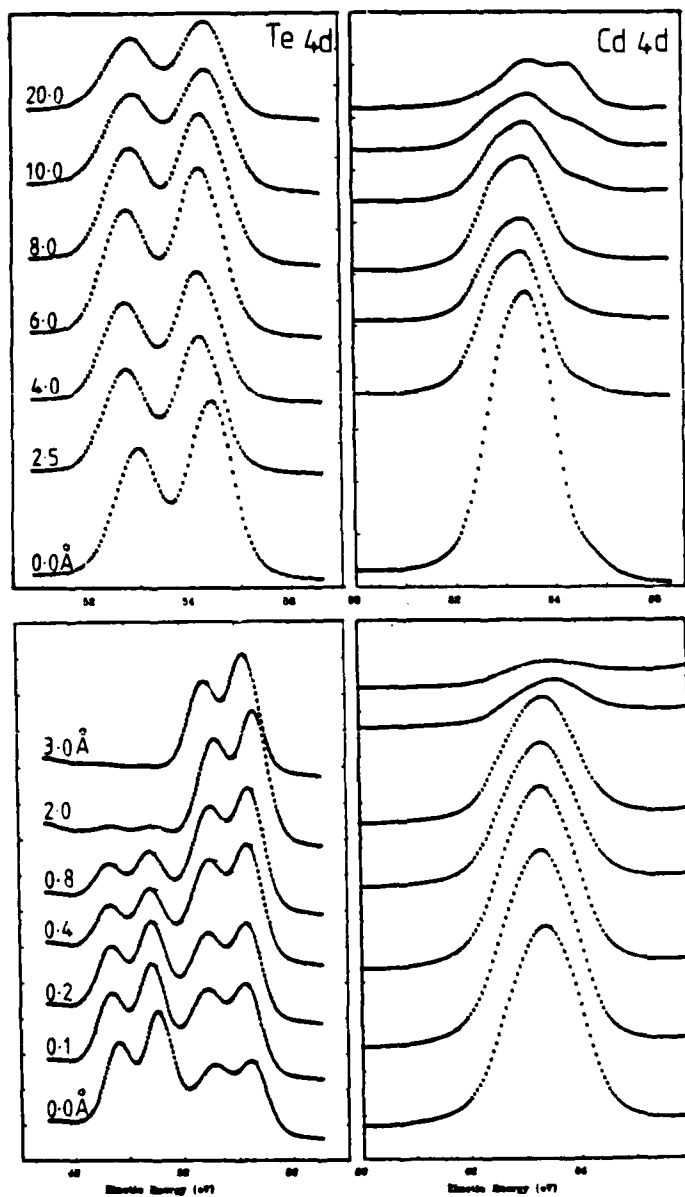


FIGURE 3



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